

WATER QUALITY MONITORING  
AND RESEARCH PLANS FOR  
KETTLE PONDS

CAPE COD NATIONAL SEASHORE

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## PREFACE

To assist in the design of a kettle pond monitoring program for Cape Cod National Seashore (CACO), the National Park Service (NPS) convened a panel of scientists and resource managers familiar with the ponds. A 2-day workshop was held on March 2-3, 1992. (See Appendix 1 for the workshop objectives and the charge to the panel.) The invited participants represented a range of disciplines including ground water hydrology; physical, biological, and chemical limnology; nutrient and geochemical processes; and freshwater ecology. Pond ecological processes and human use patterns were reviewed in the context of NPS resource management goals. Both future research needs and monitoring tasks were identified. This report presents the conclusions of the workshop panel.

## INTRODUCTION AND MANAGEMENT ISSUES

The 20 kettle ponds within Cape Cod National Seashore (CACO) are outstanding natural and recreational resources deserving priority protection by the National Park Service (NPS) (Figure 1). Their exceptional water clarity is highly valued by the public. At the same time, associated rare flora and fauna, naturally high acidity, and low nutrient levels are native characteristics that are sensitive to anthropogenic influences. (See Soukup 1977, for a general discussion of CACO kettle pond ecology; Strahler 1966, for Cape Cod geologic history; and Winkler 1989, for post-glacial pond origins and paleoecology.)

Some ponds are heavily used, both by day visitors and by seasonal residents on private land around some of the ponds. Most of the ponds have dwellings adjacent to the shorelines, which, given the unconsolidated nature of the ground water aquifer, can contribute to pond eutrophication. Some seasonal residences are being converted to year-round residences with a resulting year-round impact, especially from septic effluents, gardening herbicides and fertilizers, and eroded soils and sediments.

The NPS has collected water quality data for CACO kettle ponds for over a decade (Soukup 1977, CACO unpublished reports 1981-1992). Although this information has helped to characterize pond trophic status, a more comprehensive, systematic and intensive protocol is needed to detect important limnological changes associated with human activities.

Three key issues have emerged, each with a strong potential to alter or degrade the essential character of CACO kettle ponds:

1. **Phosphorus** and other pollutant (e.g., pathogens, organic chemicals, sediment) loading from development and recreational activities adjacent to the ponds.
2. **Acid rain** effects to pH, alkalinity and sulfur and phosphorus cycling.
3. **Liming** ponds to increase pH (decrease acidity) for enhanced recreational fishing.

Phosphorus (P) is the nutrient most likely limiting primary production and controlling water clarity in CACO's kettle ponds (Soukup 1977). Local glacial outwash soils are low in P, probably explaining the native clarity of most ponds.

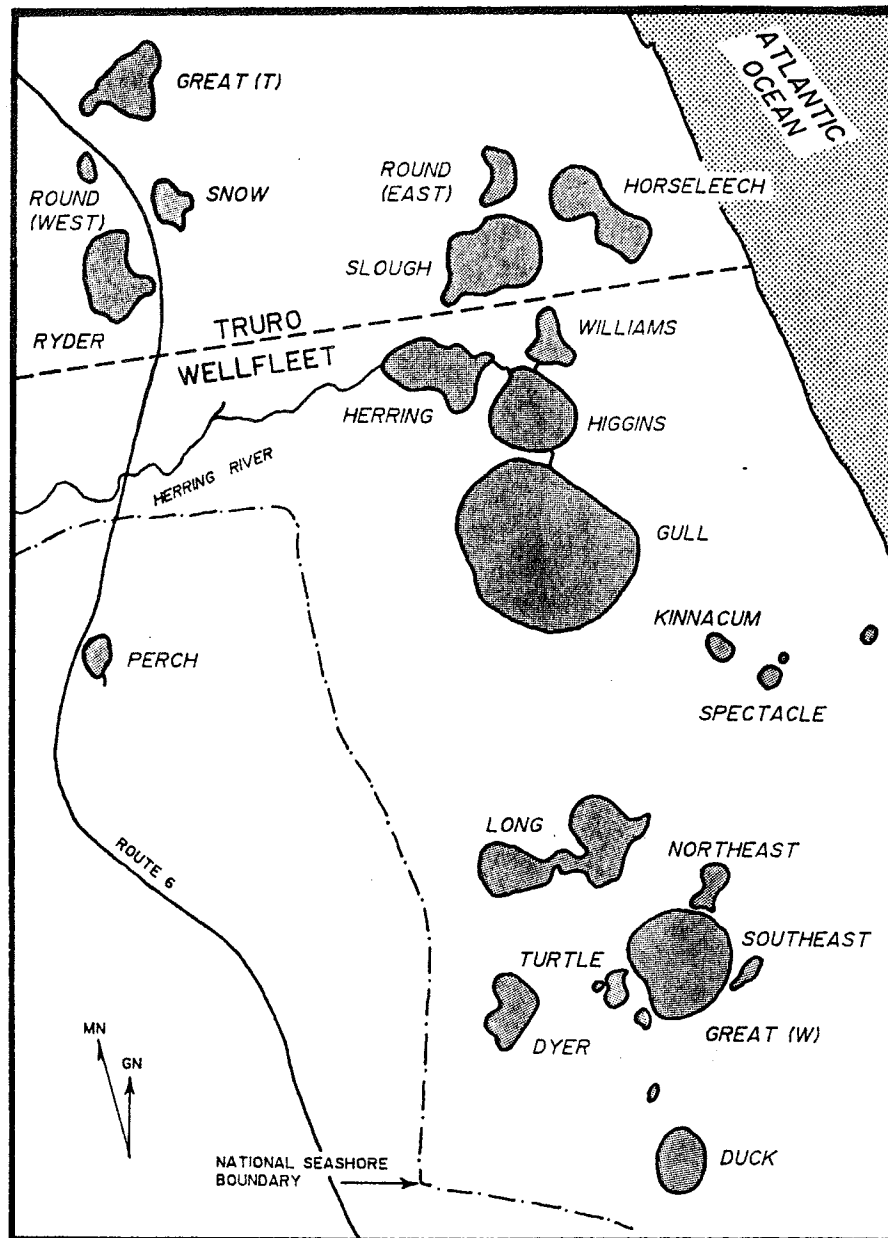


Figure 1. Kettle ponds at Cape Cod National Seashore (from Soukup 1977).

Although acid rain can have a strong potential to alter pond water quality, through acidification or disturbance to sedimentary sulfur, iron and phosphorus chemistry (Caraco et al. 1989), remedial management actions must be implemented at a regional, national, or global scale. Besides continuing to monitor pH and alkalinity of kettle ponds on a quarterly basis, in cooperation with the statewide Acid Rain Monitoring Project (ARM), no specific research or monitoring programs for acid rain effects are proposed.

Pond liming, conducted in the past by state fisheries managers at several outer Cape Cod ponds and proposed for others, is opposed by NPS managers as inappropriate for the preservation of these naturally acidic and oligotrophic aquatic systems. Paleolimnologic research has shown that the current high acidity level of land-locked ponds has been the normal condition since their formation, approximately 11,000 years before present. NPS scientists are also concerned that additions of  $\text{CaCO}_3$  could alter the species composition of both phyto- and zooplankton, increase water column production and reduce hypolimnetic aeration during periods of stratification.

A primary management concern, and the working hypothesis of this monitoring program, is that kettle pond water quality deteriorates when "extra-watershed" P is imported into the pond basin by humans. Transport by precipitation is minor (National Acid Deposition Program [NADP] data); wildlife (bird) contributions are probably important for only Gull Pond at this time (Portnoy and Soukup 1990), which is heavily used by gulls. With increasing shoreline development, cottage occupancy and pond use, humans introduce additional P to pond nutrient budgets as septic wastes, yard fertilizer, and as runoff from disturbed (denuded) shoreline soils. Human wastes, e.g., from septic systems, are assumed to be the major source of P.

Because the cycling of P includes no important gaseous form, once imported into a lake watershed this element tends to remain there. Once in the pond system, most P is adsorbed to iron in the sediments, where it remains unless released mechanically or chemically during hypolimnetic oxygen depletions.

Oxygen depletions are common in deep lakes, including several CACO ponds, where high nutrient loads increase the "rain" of organic matter to poorly circulated bottom waters. High nutrient loading leads to high algal production; leads to increased organic loading; leads to hypolimnetic oxygen deficits; leads to the reduction of sedimentary iron; and leads to increased  $\text{PO}_4$  release which, after water column mixing, can feedback to further promote algal production (see Appendix 2).

In order to address the key management issues, the long-term human influences on nutrient-limited pond processes must be described. With the identification of control factors and an understanding of their impact on degradation, it will be possible to recommend appropriate management actions and solicit public support for effective implementation.

A monitoring and research program is needed to characterize the present day trophic status of the ponds, to detect both subtle and dramatic changes in pond water quality over time, and to determine the causes of any observed changes in pond water quality or trophic status. The monitoring and research program presented here defines monitoring objectives, identifies field sampling protocols (frequency and variables), and identifies suitable laboratory methods and field instrumentation. Data management, QA/QC, data interpretation and reporting, and identification of resource management actions are all part of implementing the plan.

Importantly, this monitoring plan is not intended to be static. It is expected that methods and sampling strategies will be periodically reviewed in light of field observations, and refined to more accurately answer important management questions, while always including comparable measurement methods.

## MONITORING OBJECTIVES

In anticipation of future human impacts on pond water quality, this monitoring program purports to:

1. Characterize the trophic status of the ponds;
2. Recommend and implement methods of monitoring trophic status and limnological processes to detect important changes;
3. Describe pond-specific and seasonal in-lake and hydrological processes affecting water quality;
4. Identify and design management actions to mitigate anthropogenic effects.

To accomplish these objectives, both limnological and hydrological data are needed to answer some outstanding scientific questions. Monitoring must, therefore, include scientific research to describe in-lake biogeochemical processes sensitive to nutrient supply and to produce hydrologic data for interpretation of the role of ground water transport of nutrients to and from ponds.



# LIMNOLOGICAL MONITORING

## Previous Studies

The general ecology and limnology of the kettle ponds have been described by Soukup and Ludlum (1976), Soukup (1977), and Soukup (1979). MacCoy (1958) studied the zooplankton of Duck Pond. Winkler (1985a) reported on the post-glacial vegetation surrounding Duck Pond and later (Winkler 1985b, 1988, 1989) expanded her sediment analyses to include the paleolimnology (especially pH trends) of Duck, Great (Wellfleet), Dyer, and Great (Truro) Ponds. At present, Winkler (in preparation) is studying the paleolimnology and trends toward present eutrophication of Gull, Higgins, Herring and Williams Ponds. Portnoy and Soukup (1990) estimated phosphorus contributions to Gull Pond from various sources including migratory birds. Previous water quality monitoring efforts at CACO kettle ponds are summarized in Table 1.

## General Water Quality

The kettle ponds at CACO fall into two groups: oligotrophic, highly acidic (ca. pH 4-5) landlocked ponds, and mesotrophic, higher pH (ca. pH 6) interconnected ponds of the Gull Pond complex. This latter group, including Gull, Higgins, Williams, and Herring Ponds, discharge into the Herring River estuary and show a greater marine (or ground water) influence with higher conductivity and alkalinity than landlocked ponds (Table 2). Figure 2 shows the range of pH values in kettle ponds in January 1992. Data clustered at the left side of the histogram, pH = 4.25 to 5.25, are from landlocked, unlimed ponds. Data at the right side of the histogram, pH > 5.5 are from ponds that are interconnected with the Herring River system or have been limed for fisheries management.

Regular quarterly monitoring of pH, alkalinity and ionic composition has been conducted in cooperation with the ARM program at most ponds since 1983. Shoreline grab samples are collected by volunteers, tested for pH and alkalinity at the CACO laboratory, and for major ions by the University of Massachusetts, Department of Inorganic Chemistry. Data from this program show that pH in some ponds is very stable (Duck, Round West, Gull, Spectacle, Long, Great [Wellfleet], Higgins), some ponds show large seasonal variability (Williams, Horseleech), and some ponds show distinct downward trends (Ryder, Round East). Plots of pH changes with time are shown in Appendix 3.

TABLE 1. History of Cape Cod National Seashore kettle pond monitoring.

YEARS	PONDS	SEASONS	FREQUENCY	PARAMETERS	BY
1956-57	Duck	summer		secchi light profiles zooplankton	MacCoy (1958)
1975-76	all	spring summer	sporadic	chlorophyll secchi oxygen light temperature conductivity total P	Soukup (1977)
1980-81	Duck Gull	all	monthly	secchi light temperature conductivity	CACO
1984-86	Ryder Great (T)	all	monthly	secchi light temperature conductivity pH alkalinity oxygen major ions plankton benthos	Shortelle & Colburn (1987)
1984-92	all	all	quarterly	pH alkalinity major ions	ARM Project
1986-88	Duck Great (W) Great (T) Dyer Gull Slough Long	all	monthly	secchi temperature light conductivity	CACO

Continued

TABLE 1. History of Cape Cod National Seashore kettle pond monitoring.

YEARS	PONDS	SEASONS	FREQUENCY	PARAMETERS	BY
1987	Dyer Great (T) Great (W) Gull Slough Duck Long	summer	weekly	chlorophyll	CACO
1988-91	Dyer Great (T) Great (W) Gull Slough Duck Long	summer	weekly	secchi temperature conductivity oxygen (during stratification)	CACO

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Water clarity, as measured by secchi disk readings, varies both from pond to pond, and seasonally. Typical values range from about 6 to 10 meters. Variability in secchi disk readings obtained from 1988-1992 summer monitoring sessions at Gull and Duck Ponds, is shown in Figures 3 and 4. Compared to summer 1975 values reported by Soukup (1977, Figure 17), both Gull and Duck Ponds have decreased water clarity, at present. The deeper ponds are thermally stratified in summer. Stratification leads to hypolimnetic oxygen depletion, likely releasing phosphorus along with reduced iron and, in some ponds where iron is depleted, sulfides from the sediment.

The NPS has a long-standing concern for nutrient loading to these ponds. However, data on total water column nutrients or measurements of reduced iron and sulfur release are scarce. Importantly, the proposed monitoring and research program represents the first effort to document seasonal water column nutrient status of these ponds.

Table 2. General characteristics of Cape Cod National Seashore kettle ponds. Conductivity data are from April 1982, but have changed little. pH and alkalinity data are from January 1992. Chlorophyll data are from single observations scattered through the summers of 1975 and 1976 (Soukup 1977).

Pond	Max. depth	Area (m)(ha)	Conductivity (umhos/cm)	pH	Alkalinity (ppm)	Chloro. <i>a</i> (mg/m <sup>3</sup> )	Shore dwellings	Public beach	Land- locked
DUCK	18	5.1	97	4.8	-0.5	0.1	1	Y	Y
DYER	10	4.8	85	4.6	-1.0	0.9	3	Y	Y
GREAT (W)	15	17.5	115	4.6	-0.4	0	8	Y	Y
LONG	15	15.0	85	4.6	-0.8	1.8	22	Y	Y
TURTLE	2	1.6	86	---	---	3.6	2	N	Y
NORTHEAST	--	1.7	102	5.0	-0.4	1.5	3	N	Y
SOUTHEAST	4	1.1	108	4.9	-0.3	1.4	1	N	Y
SPECTACLE	7	0.5	110	5.0	0.1	2.4	0	Y	Y
KINNACUM	2	0.8	80	4.4	---	5.3	1	N	Y
GULL	19	44.0	119	6.5	2.9	7.6	21	Y	N
HIGGINS	6	11.3	119	6.5	3.6	6.4	7	N	N
HERRING	4	8.1	118	6.4	3.2	9.2	2	N	N
WILLIAMS	2	3.6	122	5.3	0.4	18.8	3	N	N
SLOUGH	8	11.9	122	4.7	-0.9	1.8	9	N	Y
HORSELEECH	5	10.0	146	5.3	-0.1	2.1	4	N	Y
ROUND (east)	8	2.6	108	4.8	-0.4	2.6	1	N	Y
RYDER	10	8.3	113	4.2	---	13.3	7	N	Y
SNOW	8	2.3	79	5.2	0.3	---	0	Y	Y
ROUND (west)	9	0.8	71	4.8	-0.1	---	0	N	Y
GREAT (T)	11	7.0	130	5.7	0.5	5.0	6	N	Y

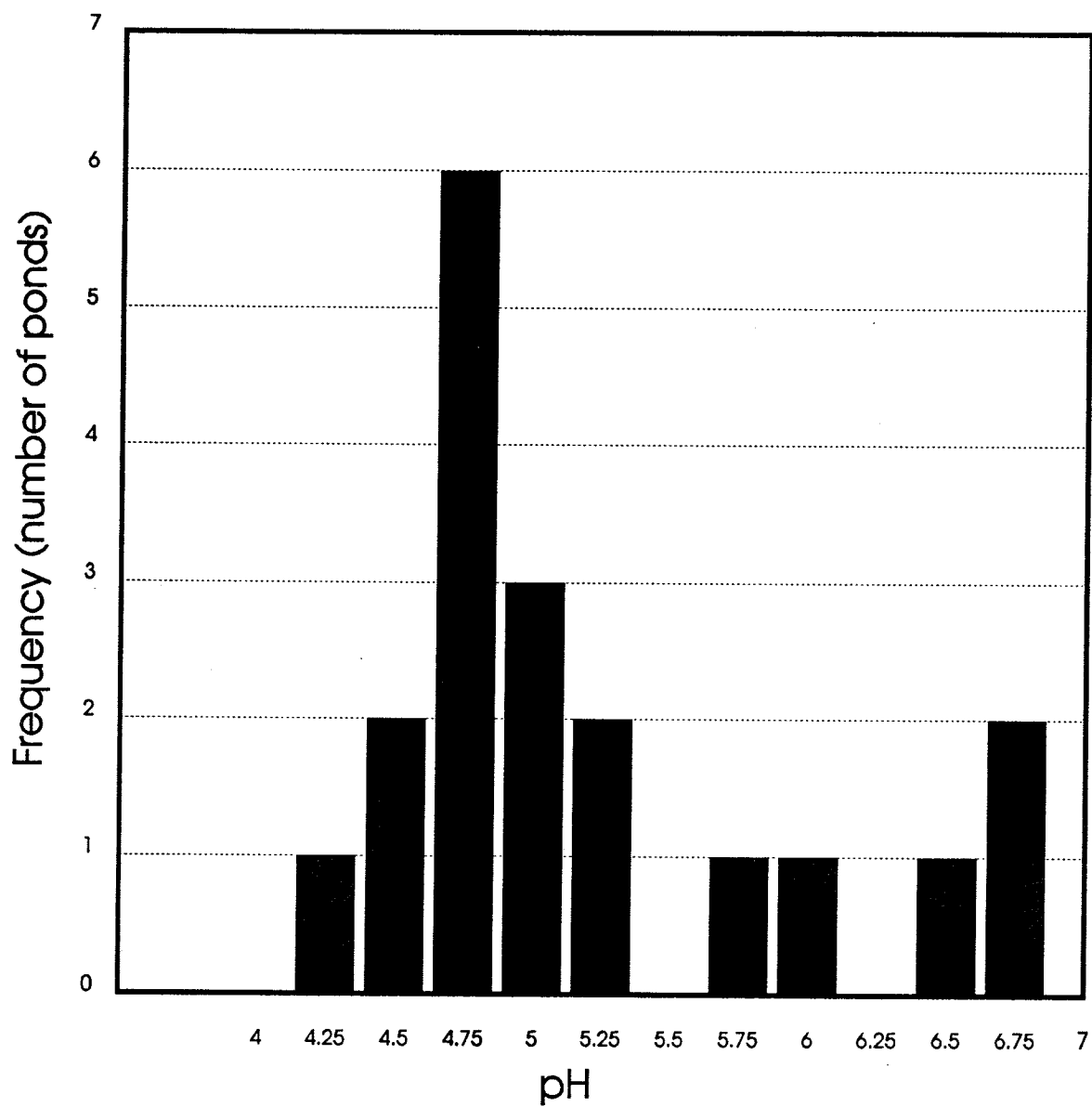


Figure 2. pH frequency distribution for Cape Cod National Seashore kettle ponds. Water samples were collected on January 26, 1992, at a 0.5 m depth, and pH was determined within 24 hours.

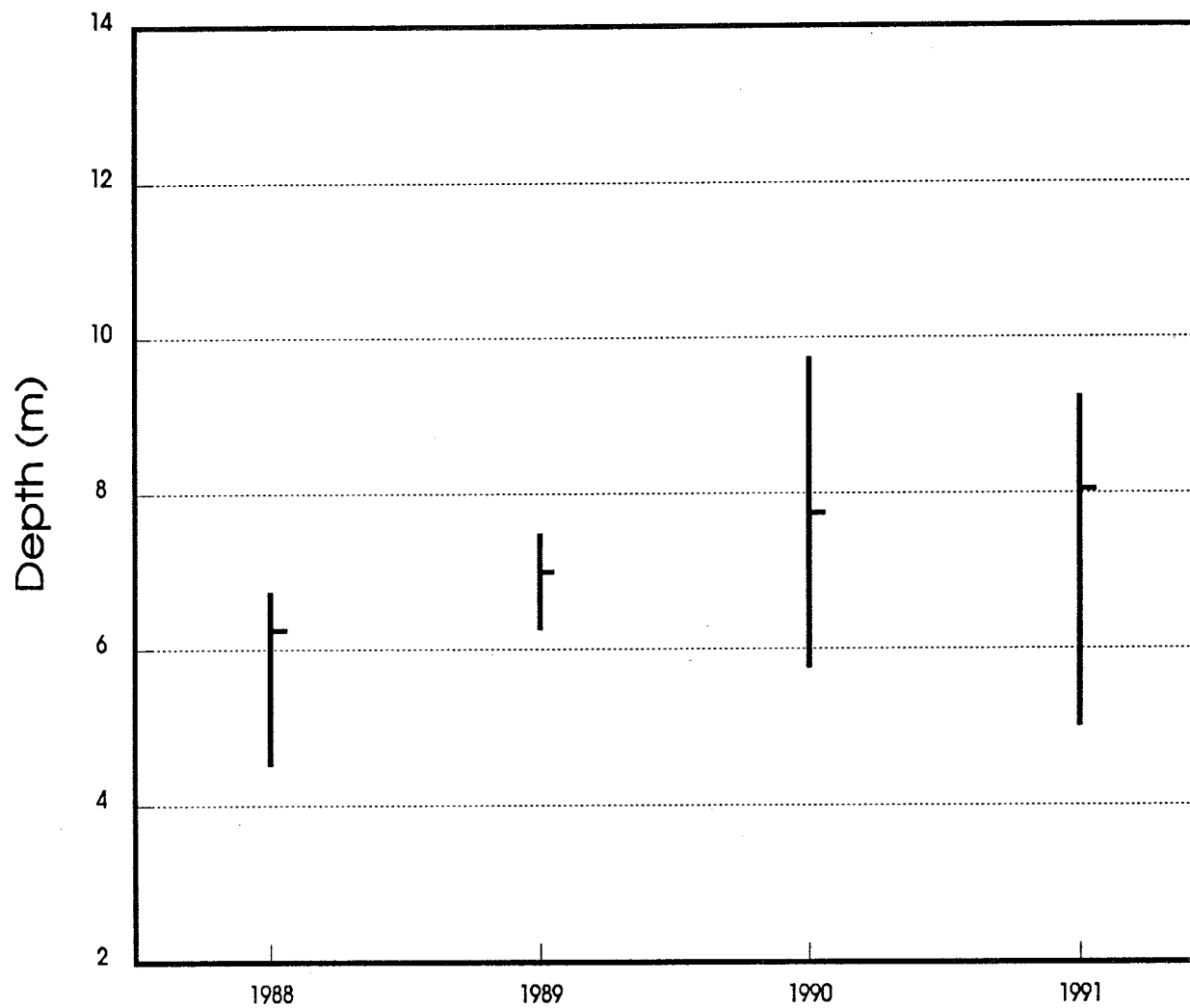


Figure 3. Annual mean and range secchi depth for Gull pond, Cape Cod National Seashore. Data were collected weekly between June and September.

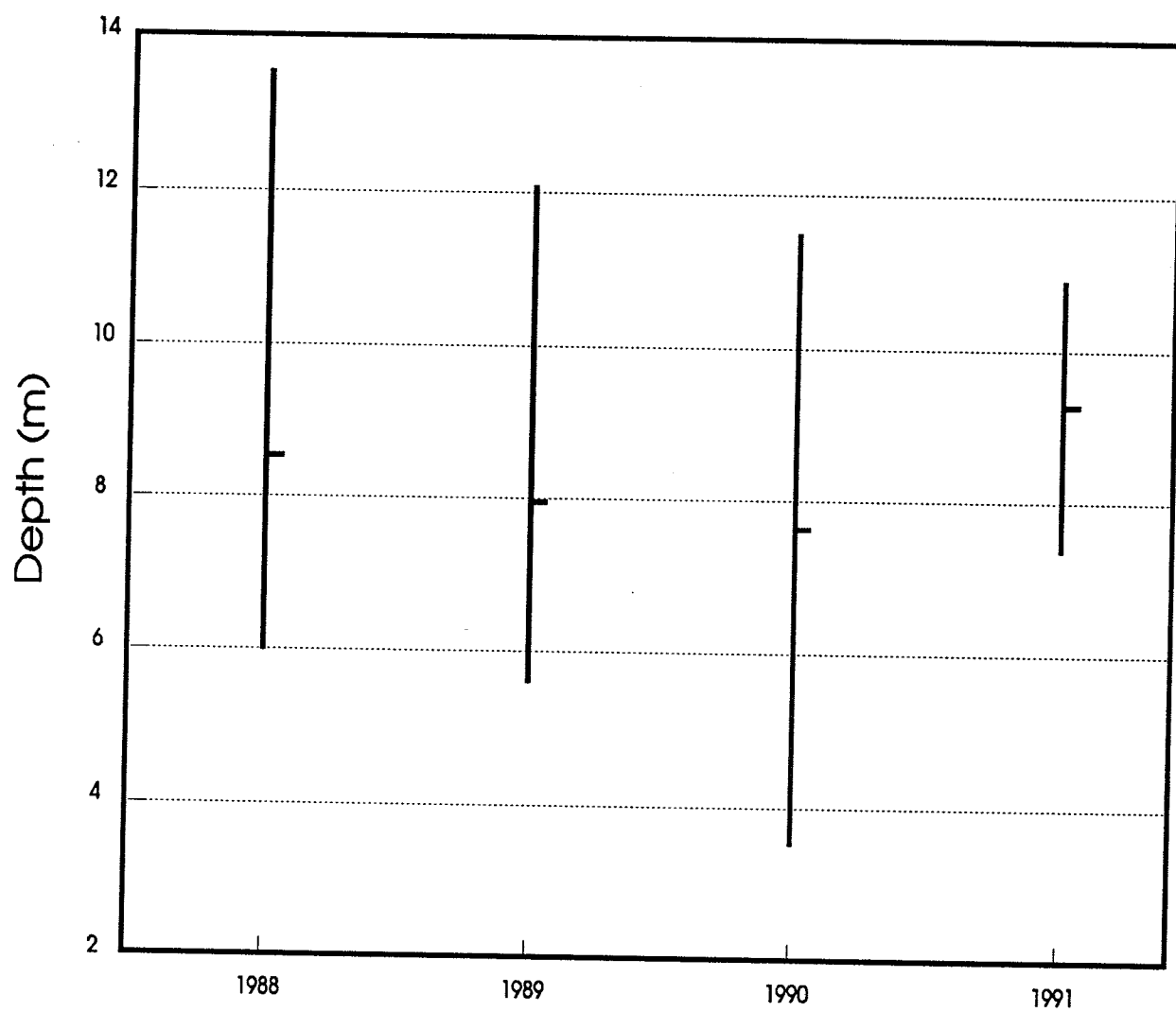


Figure 4. Annual mean and range secchi depth for Duck pond, Cape Cod National Seashore. Data were collected weekly between June and September.

## Proposed Monitoring Program

### *Study sites and frequency:*

Initially, because of staff and funding constraints, all 20 ponds will be surveyed only once annually, for nutrients and major cations and anions. This annual collection will be done in April to take advantage of conditions during normally complete vernal mixing. At this time, surface (0.5 meters [m]) grab samples are assumed to represent both nutrient status and ionic composition for the entire water column. Bottom water samples (0.5 m from the sediment) will be collected concurrently to test this assumption.

To better characterize seasonal pond processes, five of the 20 ponds have been selected for more intensive biweekly monitoring throughout the period of annual pond stratification, approximately late-May through at least August. These ponds are Duck, Gull, Ryder, Spectacle, and Great (Truro) ponds. Although each pond must be considered a unique system, the above five have been selected to represent the range in morphometry (depth and area), anthropogenic impact, and surface hydrology (isolated or interconnected). Further, the paleolimnology of all but Spectacle has, or will soon be, detailed by sediment core analysis, providing a detailed historic context. By understanding these ponds it is expected that generalizations to all ponds can ultimately be made.

Duck Pond is representative of a small (5.1 hectare [ha]), deep (18 m) pond with limited development along the shoreline. Also, a historical water quality database for Duck Pond exists (see Table 1). Gull Pond is large (44 ha), deep (19 m), and heavily used with extensive residential development; Gull Pond is part of the interconnected chain of ponds associated with the Herring River basin. Ryder Pond, of moderate area (8.3 ha) and depth (10 m), was selected because it has shown a 2-unit pH decline since the mid-1980s (see Appendix 3).

Further, there are detailed chemical and biological data for Ryder Pond from the beginning of the pH decline in 1985 (Shortelle and Colburn 1987). Spectacle Pond was selected as being representative of a small (0.5 ha), shallow (7 m), landlocked pond with no dwellings. Great Pond (Truro) is of medium size (7 ha) and depth (11 m), and was selected because it has been limed repeatedly and as recently as 1985, and has some detailed chemical and biological data (Shortelle and Colburn 1987).

All limnological measurements will be made from a small boat at a marked station at the pond's deepest point. For ponds with two or more distinct basins (Ryder and Great, in Truro), it will be necessary to establish stations at



the deepest point in each basin. For both the 20-pond spring sampling, and the summer biweekly, 5-pond sampling, field-measured variables will be measured at 1-m depth intervals. Laboratory analyses will be conducted for the surface and bottom samples taken in April, and for 7 to 8 specific depth "stations" in each of the five ponds sampled throughout the summer. (See below, and Tables 3 and 4 for field and lab variables, Table 4 for pond-specific depth stations.)

*Variables and measurement methods:*

Detailed collection, storage and analytical protocols for both field- and lab-measured variables are contained in Appendix 4. These methods will be regularly updated and improved based upon monitoring experience and concurrent research.

Monitoring variables are chosen to document important limnological processes that are closely linked to nutrient status (i.e., water column nutrients, algal production, and hypolimnetic anoxia, reduced iron and sulfides).

At *all* pond visits, temperature, conductivity (corrected to a standard 25° C temperature), dissolved oxygen, light intensity (percent of surface illumination), and chlorophyll concentration (interpreted from measured fluorescence) will be determined in the field at 1-m intervals. The secchi depth will also be recorded. For all field-measured variables, readings will be taken every 0.5 m through depth intervals of accelerated change.

The spring sample collection from all twenty ponds will include both surface and bottom water collections (0.5 m from surface and bottom) for laboratory analyses of total nitrogen (TN), and total phosphorus (TP), total sulfide, ferrous iron, pH, alkalinity (double endpoint), and the major ions (Na, Ca, Mg, Fe, SiO<sub>2</sub>, SO<sub>4</sub>, NO<sub>3</sub>, PO<sub>4</sub>, NH<sub>4</sub>, HCO<sub>3</sub> and Cl).

The summer intensive, multiple-depth monitoring of five ponds will include laboratory analyses of TN, NO<sub>3</sub>, NH<sub>4</sub>, TP, total sulfides, and ferrous iron.

The measurement of pH, alkalinity and the major ions will be limited to the quarterly ARM program of surface grab samples for all ponds. The rationale for selected field variables is as follows:

**TEMPERATURE.** Temperature is measured along with electrical conductivity (specific conductance) to follow thermal stratification of the water column. Water masses of different temperature and, thus, density can stratify with little mixing

Table 3. Proposed annual survey of CACO kettle pond water quality during spring mixing.

**Ponds:** All twenty.

**Season:** April.

**Depth stations for field variables:** 1-m intervals.

**Depth stations for laboratory variables:** 0.5 m from surface and bottom.

**Field variables:**

- Temperature, conductivity, dissolved oxygen by Hydrolab
- Chlorophyll fluorescence by field fluorometer
- Light by Licor meter with deck cell
- Secchi depth

**Laboratory variables:**

- Dissolved oxygen (DO) by Winkler titration for low DO bottom waters
- $\text{Fe}^{++}$  by Ferrozine method
- Total sulfides using DPDH indicator
- Total P by acid persulfate digestion and ascorbic acid method for  $\text{PO}_4$
- Total N by alkaline persulfate digestion and cadmium reduction for  $\text{NO}_3\text{-NO}_2$
- Ammonium-N by the phenolate method
- Nitrate-nitrite-N by cadmium reduction
- Phosphate by the molybdate blue method
- Anions by ion chromatography
- Cations by inductively-coupled plasma emission spectroscopy

**Table 4.** Proposed summer limnological monitoring of selected CACO kettle ponds.

**Ponds:** Gull, Duck, Ryder (both basins), Spectacle, and Great - Truro (both basins).

**Temporal frequency:** Biweekly

**Season:** Summer stratification. Tentatively May through October.

**Depth stations for field variables:** 1-m intervals.

**Depth stations for laboratory variables:** (Sf & B mean 0.5 m from surface and bottom, respectively)

Duck: Sf, 1, 3, 6, 9, 12, 15, B

Gull: Sf, 1, 5, 8, 11, 14, 17, B

Ryder: Sf, 1, 3, 5, 7, 9, B

Spectacle: Sf, 1, 3, 5, B

Great (Truro): Sf, 1, 3, 5, 7, 9, B

**Field variables:**

- Temperature, conductivity, dissolved oxygen by Hydrolab
- Chlorophyll fluorescence by field fluorometer
- Light by Licor meter with deck cell
- Secchi depth
- Water level

**Laboratory variables:**

- Dissolved oxygen by Winkler titration for low DO bottom waters
- Fe<sup>++</sup> by Ferrozine method
- Total sulfides using DPDH indicator
- Total P by acid persulfate digestion and ascorbic acid method for PO<sub>4</sub>
- Total N by alkaline persulfate digestion and cadmium reduction for NO<sub>3</sub>-NO<sub>2</sub>
- Ammonium-N by the phenolate method
- Nitrate-nitrite-N by cadmium reduction
- Phosphate by the molybdate blue method

between layers during summer months leading to stagnant, and often oxygen-poor, conditions in bottom waters. Temperature profiling describes the relative thermal resistance to mixing. Anoxia induces the chemical reduction of iron and the release of sedimentary phosphorus and sulfides into the water column. Phosphorus release can trigger algal blooms, if transported to well-lit depths, and sulfides are toxic to aquatic life. Temperature profiles are also basic to evaluating ground water inputs and outputs, and for computing heat budgets.

**CONDUCTIVITY.** This a gross and simple measure of the amount of dissolved substances in water. Conductivity is temperature-dependent (field readings must be later temperature-compensated) and can aid in discerning thermal, as well as chemical, stratification. Conductivity, like temperature, profiling will provide information for discerning ground water influences.

**DISSOLVED OXYGEN.** Besides being essential for aerobic respiration (and therefore critical for the survival of aquatic animals), oxygen concentrations influence all major nutrient cycles, including the storage of phosphorus in lake sediments. Lakes undergoing eutrophication typically show increases in the duration of anoxia and the vertical extent of anoxic bottom waters.

**LIGHT PENETRATION.** A light meter is used to measure incident light (visible range) above the lake surface and at specific depths, preferably simultaneously, to calculate the percent transmission through the intervening water column. Photosynthesis and aquatic plant production are dependent upon available light: thus, photosynthetic oxygen production is often limited by light transmission to the bottom waters of turbid lakes. This phenomenon can exacerbate deep-water oxygen depletions. Light profiles can also show where planktic organisms are concentrated.

**FLUORESCENCE.** (Profiles and depth-specific measurements) Chlorophyll compounds fluoresce, i.e., emit long-wavelength light when illuminated with a specific shorter wavelength. This feature is used to measure chlorophyll concentration in water as an indicator of algal density (i.e., primary production). Use of a flow-through cell in a field fluorometer provides a large number of real-time and time-averaged *in situ* measurements. High

concentrations are observable in the field, allowing intensive, depth-specific resampling, collections and subsequent species identifications. Phytoplankton are the most important primary producers in deep lakes, and are one of the first ecosystem components to respond to anthropogenic nutrient loading.

**SECCHI DEPTH.** A single measurement of the maximum depth at which a white 30-cm disk can be seen is widely used as an index of clarity.

*Discussion:*

Among the laboratory-measured variables, the measurement of total nutrients is essential for assessing nutrient status and for understanding seasonal processes affecting nutrient availability to plant production. Reduced iron and sulfur are key indicators of hypolimnetic oxygen stress and nutrient regeneration from the sediment. See Appendix 2 for a discussion of lake biogeochemical processes. pH, alkalinity (acid neutralizing capacity), major cations and anions need to be monitored for the assessment of ground water flow as well as various changes associated with acid-base chemistry (e.g., acid deposition effects and the potential mobilization of toxic metals).

A portable water quality monitoring instrument (Hydrolab Surveyor 3) will be used for the field measurement of temperature, conductivity, pH, and dissolved oxygen. This instrument will be calibrated every two weeks as follows: temperature - calibrated mercury thermometer; conductivity - NADP standard at 25° C; pH - NADP standard; dissolved oxygen - Winkler titration. For oxygen concentrations below 2 parts per million (ppm) (e.g., in bottom waters where H<sub>2</sub>S may interfere), samples will be collected for laboratory titration.

Light readings will be made using a LiCor meter with deck cell. Fluorescing chlorophyll concentrations will be determined with a Turner Designs fluorometer, standardized daily with chlorophyll standards. Secchi depth readings will also be made and recorded.

After profiling and secchi depth readings are completed, water samples for chemical analyses will be collected with a vertical Kemmerer sampler. All variables should be measured from aliquots drawn from the same bottle collection. Samples for total sulfides and ferrous iron will be fixed immediately in the field with zinc acetate and hydrochloric acid, respectively. A 250 milliliter (ml) aliquot for both total N and P will be frozen until analysis using the CACO autoanalyzer. Samples for Winkler determinations of DO will be immediately fixed with manganous sulfate and alkaline iodide sodium

azide (see Appendix 4). All samples will be stored on ice during transport to the laboratory. In the laboratory, cation samples will be acidified with  $\text{HNO}_3$  to  $\text{pH} < 2$ . These, together with anion samples, will be held at  $4^\circ \text{C}$  until analyzed by an outside lab. Samples will also be collected for future analyses of phytoplankton and zooplankton communities.

Phytoplankton collections will consist of one 60-ml grab from 0.5 m below the surface, and one from the depth of maximum fluorescence, both fixed with Lugol's solution and archived for later study. Zooplankton samples will be obtained from vertical hauls through the entire vertical profile with a zooplankton net. Zooplankton samples will be preserved in glass vials with 70 percent ethanol plus a few drops of glycerin and archived for later study. Both plankton groups will be sampled at all ponds during the spring survey, and biweekly at the five ponds intensively monitored throughout the summer. Comparative analyses of species composition of the phytoplankton and zooplankton samples will be conducted by an outside contractor at some time in the future.

A staff gage will be established at each of the five intensively monitored ponds to monitor (biweekly) water level fluctuations, and to compare with adjacent ground water levels (see *Water Table Mapping* below).

#### *Data storage:*

Data will be stored in Dbase software files by park resource management staff.

## HYDROLOGIC RESEARCH

Because ground water in sediments adjacent to the ponds can freely interchange with pond water, ground water can be an important source of nutrients for Cape Cod kettle ponds. Local hydrogeologic information is needed for the interpretation of pond water and ground water exchange in order to describe limnology. Water table mapping is required to define areas of inflow and outflow around pond basins and, together with pond bathymetry, to estimate pond water residence times for the interpretation of nutrient budgets. Hydrogeologic data are needed to map relative permeabilities and hydraulic gradients that control flow direction and quantity.

Although the outer Cape aquifer is largely unconfined, clay lenses observed near and underlying some kettle ponds likely affect ground water movement

into and out of ponds. The depths of ground water inflow and outflow are important given the thermally and chemically stratified nature of the ponds in summer.

The limnological monitoring described above may, in fact, be considered an interim program which may be modified once the hydrological and chemical aspects of the pond systems are better described by this hydrologic research. The following tasks are recommended.

## **Local Hydrogeology**

Ideally, the hydrogeologic environment of all 20 ponds would be interpreted from site specific research. However, this would be an extensive task and thus, it is recommended that work be directed toward the two most-studied sites. These are Gull Pond, already surrounded by a network of multilevel piezometers, and representative of the near-neutral pH group, and Duck Pond, a good example of the acidic, land-locked kettle ponds. It is anticipated that clear hydrogeologic understanding of these ponds can be extrapolated and applied to systems analysis of other CACO ponds.

### *Geology*

Well logs are available from the U.S. Geological Survey for the Gull Pond observation well network, and perhaps from private wells near both Gull and Duck Ponds. Soil data may also be available from percolation tests conducted for the installation of shoreline septic systems. These data should be analyzed to map permeabilities, and combined with water table contours to describe flow paths.

### *Water Table Mapping*

In lieu of a detailed water table map for the entire ponds region, pond-specific water table mapping is recommended at Gull and Duck Ponds. This work should be extended to all five intensively monitored ponds as soon as funding for well drilling becomes available.

As an immediate interim measure, water levels in the existing observation wells around Gull Pond should be measured year round on a monthly basis. Pond water level monitoring, using surveyed shoreline bench marks, should be conducted between April and October to link limnological data to surface water levels at Gull, Great (Truro), Ryder, Duck and Spectacle Ponds.

## **Pond Morphometry**

Beginning with the five intensively monitored ponds, bathymetric maps of all ponds should be prepared to estimate total, epilimnetic and hypolimnetic pond volumes. Gull and Duck Ponds have completed bathymetric maps from previous studies. Data can be collected using a depth finder in summer, or a simple lead line through the ice in winter. Horizontal control is best achieved using surveying equipment on the ice in winter.

## **Water Budgets**

In general, a water budget includes estimates of pond inflow (precipitation, ground water inflow, streamflow) and outflow (evaporation, ground water outflow, streamflow). Streamflow will be an important term only for the chain of ponds associated with the Herring River basin, where sluiceways have been constructed to connect the ponds. The quantification of specific water inflows and outflows is needed to assess nutrient budgets affecting pond biogeochemical processes.

A weather station recently established at CACO Headquarters, plus the Truro NADP site, will provide needed meteorologic data for water budgets.

## **Ground Water Quality Survey at Gull Pond**

The availability of an extensive well network around Gull Pond will be exploited to assess local ground water quality. To test for gross seasonal variations, sampling will be conducted in both June (or July) and October. Variables will include: temperature, pH, alkalinity, conductivity, and all major ions. Analytical results from these samples will be interpreted to plan the timing of future ground water quality monitoring.

## **Duck Pond Hydrologic Research**

Duck Pond was identified as the second pond to be studied in an attempt to relate ground water flow and quality to pond water quality. Although a detailed research plan has not been articulated, it is anticipated that a network of shallow monitor wells will be required, installed about 20 feet landward of the shoreline. These wells could be installed by hand auguring and driving well points to 5 to 10 feet below the water table. If deeper wells are needed, a portable drill rig will probably be needed for their installation. Likewise, a drill rig would be needed if it is decided to install monitoring wells at greater distances (100 to 200 feet) from the pond.



Importantly, hydrologic studies at Gull and Duck Ponds are considered pilot projects, with methods and results to be applied to the other kettle ponds as support for research and monitoring increases.

## PROJECT MANAGEMENT, DATA ANALYSIS, AND REPORTING

During the preparation of this monitoring plan and its initial 1992 implementation, it has become obvious that the extent and complexity of the work requires a full-time program coordinator. One of two positions approved in CACO's future target organization (Hydrologist, Aquatic Ecologist, or other Water Resource Specialist) should be the staff person directing park resource management staff in field data collection and laboratory analyses. This individual would also be primarily responsible for data management and preliminary reduction and interpretation (e.g., summary plots and descriptive statistics).

A panel of experts, such as assembled for the March 1992 workshop, should be convened by the staff Water Resource Specialist on an annual basis to review and interpret the data, highlight management implications, and suggest revisions to the monitoring plan. All of those who participated in the workshop have enthusiastically indicated a continuing interest in this program.

The staff Water Resource Specialist should summarize both the monitoring data and the panel's analysis and recommendations in an annual report. The driving objective of this work will be to provide park managers with recommendations for pond management that are based on the interpretation of the most recent and comprehensive monitoring data. It is emphasized, moreover, that major decisions affecting pond management should not be made without at least five years of monitoring, or until a consensus is clear on a pond's trophic status and direction, and rate of change. This is important to avoid reacting to idiosyncratic events.

## COROLLARY STUDIES

Although beyond the scope of this water quality monitoring plan, a number of other important research projects have been identified that would compliment the proposed limnological and hydrologic work. These studies would be focused on a biological survey of the water column, benthic and

shoreline communities. Results of this work would permit comparison with both previous and future surveys. Proposed corollary studies include:

**POND MARGIN ECOLOGY.** Monitoring for macrophytes in the pond margin and wetland transition area is important for assessing the present and future trophic status of the ponds. The focus of this project is develop baseline area maps of the current distribution of macrophytes along pond shorelines, inventory the species composition and abundance (biomass and relative cover) of mapped emergent pond vegetation, study the factors (e.g., bathymetry, slope, aspect, insolation, soil) controlling the distribution of aquatic plants, and develop long-term monitoring protocols to assess and detect changes in response to potential nutrient loading at the ponds.

**BENTHOS AND SURFACE SEDIMENTS.** Baseline data on benthic invertebrates are needed to understand the biotic impacts of water quality changes associated with visitor use, adjacent residential development and fishery enhancement activities (liming, fish stocking). Surface sediment analysis would provide measures of nutrient loading (increased pyrite formation), erosion (increased organics in sediments), the productivity (and re-identification) of immersed macrophytes. In addition, sediment analysis might be less biased than monitoring biota in water samples, as these samples often represent event-scale or seasonal changes rather than whole lake changes. Data from sediment analysis and benthic invertebrate sampling could also identify important biological indicators to simplify future monitoring.

**FISH.** The fishes of kettle ponds are a somewhat unique assemblage of acid-tolerant species. Effects of the state's fishery enhancement program and changes in pond water quality can only be properly evaluated based on a comprehensive fish survey. A baseline survey of the species composition and distribution is lacking. Fish fauna are expected to vary with pond size, the extent and character of adjacent development patterns, shoreline vegetation and water quality.

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## APPENDIX 1

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### Kettle Pond Monitoring Workshop Agenda and Objectives

#### Cape Cod National Seashore

# AGENDA

## Monday, 2 March 1992

- 10:00 am Welcome and Introduction  
*Andrew Ringgold*, Superintendent  
*Charles T. Roman*, Regional Water Resources Coordinator
- 10:15 Kettle Pond Resource Management Issues  
*David Manski*, Resource Management Specialist
- 10:45 Review of Kettle Pond Water Quality Assessment and Monitoring Data  
*John Portnoy*, Park Biologist
- 11:30 Workshop Objectives  
*Larry Martin* (Workshop Moderator), Water Resources Division
- 12:00 Lunch -- Discuss morning information
- 1:00-4:30 Formulate monitoring program goals to meet resource protection needs.
- Identify specific questions or hypotheses to be answered by the program.
- Select/discuss water quality and hydrological variables and processes to be monitored.
- Initiate monitoring program design.

Dinner

## Tuesday, 3 March 1992

- 7:30-9:00 Field Trip
- 9:00 Monitoring Program Design
- 12:00 Adjourn

# Kettle Pond Monitoring Workshop

## Cape Cod National Seashore

### WORKSHOP OBJECTIVES

The broad objective of the workshop is to design a monitoring program enabling the National Park Service to characterize the present day status of the ponds, to detect subtle and dramatic changes in pond quality over time, and to determine the causes of any observed changes in pond quality.

#### **The monitoring program should;**

- Define expectations and goals of the program to insure that effective and scientifically valid management decisions can be made.
- Describe cause-effect links between human resource activity (e.g., land use alterations, nutrient loading), and expected environmental response. Based on a conceptual model, identify specific questions to be answered by the monitoring program.
- Select variables to monitor and provide a rationale for selection (e.g., primary production, water clarity, pH, nutrients, dissolved oxygen, community structure, geochemical processes, P regeneration, groundwater input, residence time).
- Provide a sampling design enabling detection of meaningful change and/or trends with some degree of certainty. Consideration must be given to sampling frequency, replication, statistical analyses, and natural variability.
- Define meaningful change for selected variables. For example "Does average summer secchi depth of less than 8 m in Great Pond represent a meaningful change warranting management action"?
- Identify field methods to employ; including instrumentation and spatial needs (e.g., surface only vs. surface-bottom profile; cross-pond transect vs. middle only).
- Identify laboratory methods.
- Identify significant gaps in our understanding of kettle pond hydrology, chemistry, and ecology and recommend research needs.

## **Workshop Product**

- During the 2-day workshop, participants will develop a detailed monitoring program outline. Prior to April 1, 1992, National Park Service staff will prepare a draft monitoring program for review by the participants.



## APPENDIX 2

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### HYPOTHESIZED BIOGEOCHEMICAL PROCESSES

Phosphorus (P) is the nutrient most likely to be limiting primary production and controlling water clarity in kettle ponds. Local glacial outwash soils are low in P, which probably explains the natural clarity of most ponds. Nitrogen is supplied by microbial fixation of atmospheric nitrogen gas in freshwater environments. It is hypothesized that kettle pond water quality deteriorates when "extra-watershed" P is imported into the pond basin by humans. Import of P by precipitation is minor (NADP data). Wildlife (bird) contributions of P are probably important for only Gull Pond (NADP data, Portnoy and Soukup 1990). With increasing shoreline development, cottage occupancy and pond use, humans provide additional P to pond nutrient budgets from septic wastes and through shore erosion. Human wastes, e.g., from septic systems, are assumed to be the major source of P.

Because P has no biogeochemically important gaseous form, once imported into a lake watershed it tends to remain there. Most P is adsorbed to iron and iron complexes in the sediments, where it remains unless regenerated mechanically or chemically during hypolimnetic oxygen depletions.

Phosphorus is supplied to the water column largely from the sediments during seasonal overturn. Under oxidizing conditions,  $\text{PO}_4$  is complexed with sedimentary ferric iron and its oxyhydroxides. With high organic loading, warm surface water temperatures and water column stratification, bacterial respiration can exceed oxygen supply. This leads to the reduction of  $\text{Fe}^{+3}$  to soluble  $\text{Fe}^{+2}$  and the liberation of soluble  $\text{PO}_4$  from the lake sediments. With overturn and renewed mixing,  $\text{PO}_4$ -enriched water is carried to well-lit surface waters where it is assimilated by phytoplankton.

Iron (Fe) is also active in the lake's sulfur cycle. Reduced iron ( $\text{Fe}^{++}$ ) precipitates the sulfides produced by anaerobic sulfate-reducing bacteria in the sediment. Sulfide precipitation may in fact, limit  $\text{PO}_4$  bonding sites on Fe complexes. Thus, the presence of free sulfides can indicate that Fe is in short supply for sulfide binding, and more importantly, for phosphate complexation. The detection of free sulfides, either by odor ( $\text{H}_2\text{S}$  at low pH) or colorimetry, is therefore indicative of high  $\text{PO}_4$  release from anaerobic sediment.

Briefly summarized, nutrient loading leads to algal production, causing increased thermal stratification and organic loading, which leads to hypolimnetic oxygen deficits. Reduction of sedimentary iron occurs, leading to increased P release which, after water column mixing, can feed back to further encourage algal production.

Nutrient additions manifest their effect in the water column; however, phytoplankton assimilation of a limiting nutrient is so rapid that little soluble

$\text{PO}_4$  will be detectable in pond water even during conditions of high loading. Therefore, persulfate digestions of whole water samples for total nitrogen (N) and P determinations will be conducted.

Increased algal productivity in kettle ponds should be evident as reduced clarity, as algal biomass increases. This can be measured directly using light transmission, secchi depth, and fluorescence chlorophyll. Secondary effects of increased algal production include reduced light transmission and increased organic loading. As the lake's surface waters become more turbid, a greater proportion of heat accumulates in the epilimnion, enhancing thermal stratification and reducing mixing.

The isolation of deep waters from atmospheric and photosynthetic oxygen, and the increased organic load from epilimnetic production, leads to hypolimnetic oxygen depletion. Thus, the systemic effects of heightened algal production will be monitored with temperature/conductivity/oxygen profiles, estimates of hypolimnetic oxygen consumption, and measurements of ferrous iron and sulfide concentration.



## APPENDIX 3

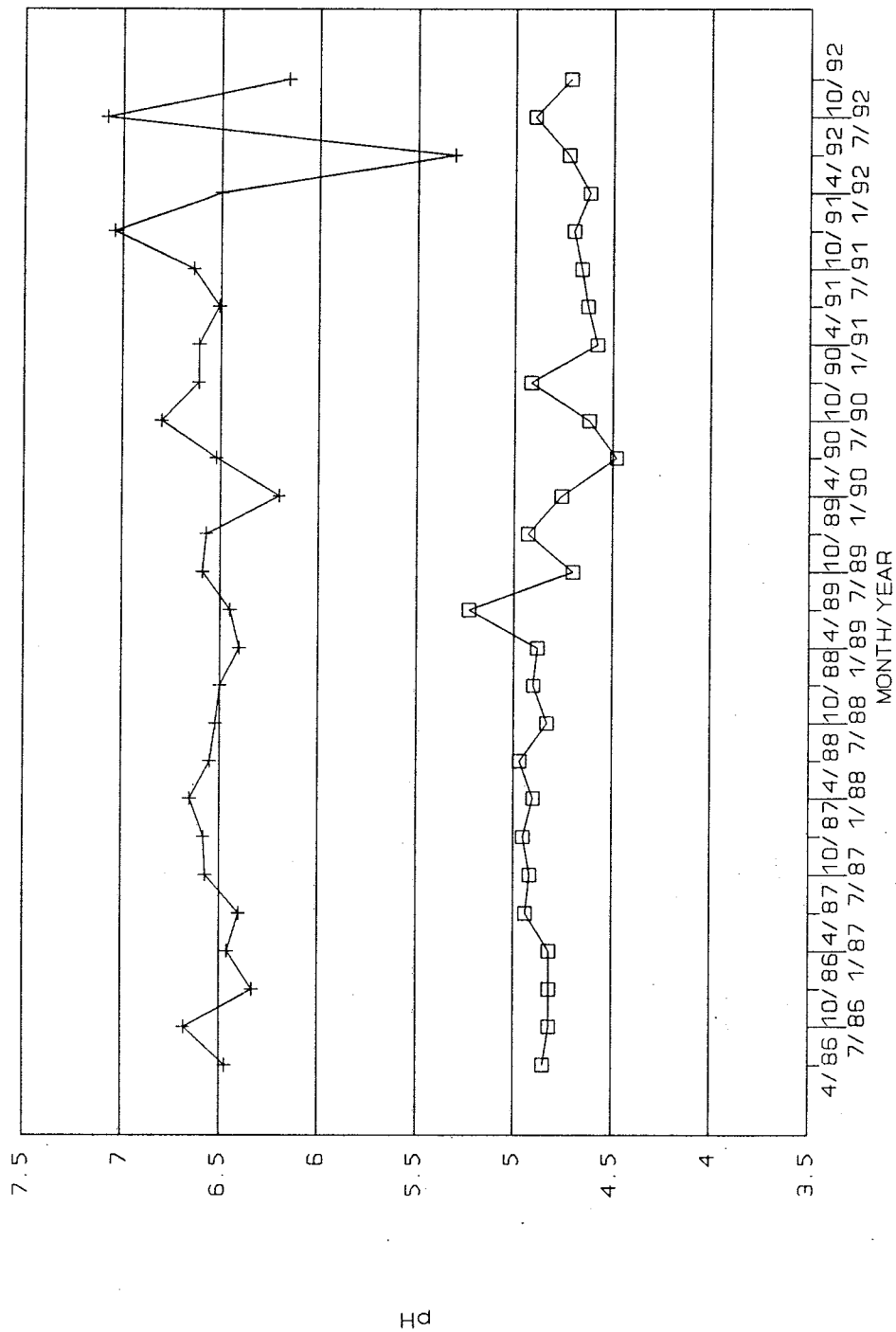
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The tables and graphs on the following pages show pH trends at Cape Cod National Seashore kettle ponds from 1983 to 1992. Water samples were collected quarterly at a 0.5 m depth. pH was determined within 24 hours.

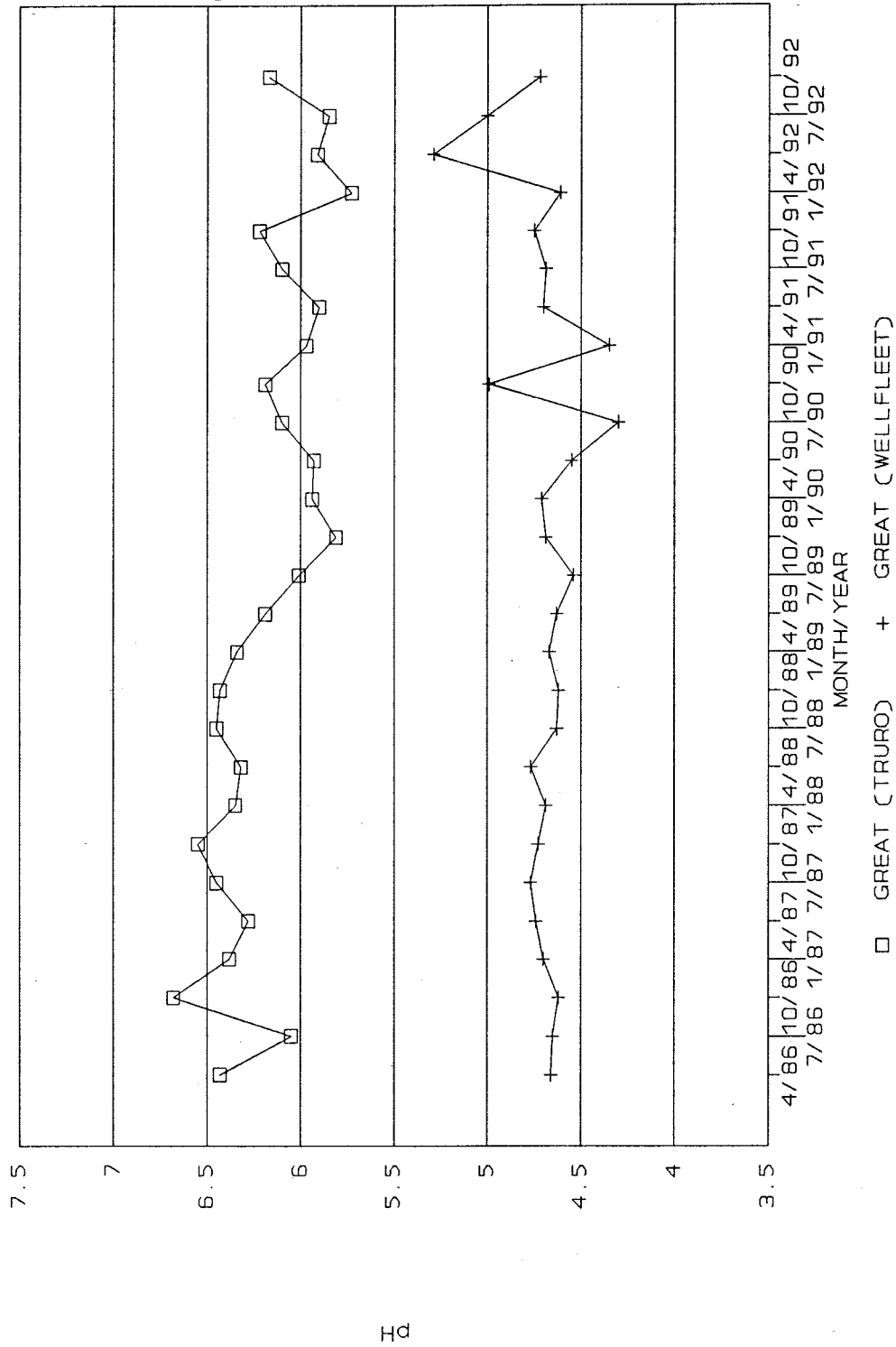
	DUCK	DYER	GREAT (TRURO)	GREAT (WELLFLEET)	GULL	HERRING	HIGGINS	HORSE- LEECH	KINN- ACUM	LONG
OCTOBER 1985					6.59		6.42			4.63
JANUARY 1986					6.73		6.54			4.47
APRIL 1986	4.71	4.85	6.43	4.66	6.65	6.28	6.47	5.85	4.60	4.56
JULY 1986	4.66	4.82	6.05	4.65	7.16	6.67	6.68	6.44	4.52	4.60
OCTOBER 1986	4.72	4.82	6.68	4.62	6.65	6.47	6.33	6.28	4.40	4.60
JANUARY 1987	4.68	4.82	6.38	4.70	6.55	6.40	6.46	5.65	4.64	4.68
APRIL 1987	4.76	4.94	6.28	4.74	6.35	6.20	6.40	5.69	4.65	4.74
JULY 1987	4.64	4.92	6.45	4.77	7.22	6.99	6.57	6.19	4.52	4.71
OCTOBER 1987	4.76	4.95	6.55	4.73	6.55	6.56	6.58	6.07	4.52	4.72
JANUARY 1988	4.64	4.90	6.35	4.69	6.69	6.35	6.65	5.45	4.60	4.65
APRIL 1988	4.69	4.97	6.32	4.77	6.60	6.50	6.55	5.42	4.62	4.76
JULY 1988	4.61	4.83	6.45	4.63	6.80	6.44	6.52	6.05	4.40	4.66
OCTOBER 1988	4.75	4.90	6.43	4.62	6.32	6.45	6.50	6.26	4.38	4.60
JANUARY 1989	4.58	4.88	6.34	4.67	6.36	6.45	6.40	5.42	4.50	4.59
APRIL 1989	4.61	5.23	6.19	4.63	6.51	6.35	6.45	5.20	4.43	4.56
JULY 1989	4.69	4.70	6.01	4.54	6.70	6.73	6.59	6.01	4.31	4.51
OCTOBER 1989	4.80	4.93	5.81	4.69	6.71	6.76	6.57	6.31	4.40	4.55
JANUARY 1990	4.77	4.76	5.94	4.71	6.62	6.33	6.20	5.17	4.61	4.67
APRIL 1990	4.57	4.48	5.93	4.55	6.57	6.35	6.52	5.64	4.25	4.41
JULY 1990	4.51	4.62	6.10	4.30	6.76	6.33	6.80	6.30	3.98	4.43
OCTOBER 1990	5.00	4.92	6.19	4.99	6.74	6.66	6.61	6.38	4.74	4.99
JANUARY 1991	4.80	4.58	5.97	4.35	6.60	6.88	6.61	5.71	4.62	4.69
APRIL 1991	4.75	4.63	5.90	4.70	6.61	6.53	6.51	4.76	4.45	4.70
JULY 1991	4.81	4.66	6.10	4.69	6.77	6.90	6.64	5.99	4.31	4.60
OCTOBER 1991	4.86	4.70	6.22	4.75	6.51	7.03	7.04	6.24	4.39	4.69
JANUARY 1992	4.77	4.62	5.73	4.61	6.53	6.43	6.50	5.30	4.41	4.55
APRIL 1992	4.82	4.73	5.91	5.29	6.64	6.50	5.31	5.26	4.53	4.67
JULY 1992	4.86	4.90	5.85	5.00	6.90	6.91	7.08	5.80	4.49	4.80
OCTOBER 1992	4.79	4.72	6.17	4.72	6.52	6.60	6.16	6.19	4.34	4.66

	NORTH- EAST	ROUND WEST	ROUND EAST	RYDER	SLOUGH	SNOW	SOUTH- EAST	SPECTACLE	WILLIAMS
OCTOBER 1985				5.82					
JANUARY 1986				5.60					
APRIL 1986	4.80	4.90	5.56	5.24	4.98	6.69	4.85	5.40	5.56
JULY 1986	4.68	4.79	4.18	5.55	5.03	6.02	4.73	5.20	6.60
OCTOBER 1986	4.64	4.94	5.76	5.70	4.87	5.95	4.80	5.01	6.10
JANUARY 1987	4.84	5.03	5.77	5.34	4.80	5.56	4.93	5.18	5.22
APRIL 1987	4.91	5.00	5.54	5.28	4.90	5.73	5.03	5.19	6.06
JULY 1987	4.57	4.48	5.52	5.08	4.70	5.29	4.94	5.05	7.45
OCTOBER 1987	4.86	4.80	5.65	5.57	4.83	5.67	5.03	5.00	6.51
JANUARY 1988	4.77	4.96	5.43	5.22	4.75	5.73	4.97	5.05	5.54
APRIL 1988	4.77	4.93	4.77	5.14	4.76	5.48	5.14	5.05	6.03
JULY 1988	4.56	4.72	5.34	4.96	4.56	5.51	4.83	4.88	6.69
OCTOBER 1988	4.66		5.46	5.31	4.60	5.76	4.91	4.95	6.30
JANUARY 1989	4.95	4.72	5.36	5.10	4.69	5.34	4.93	4.95	4.61
APRIL 1989	4.98	4.62	5.25	4.68	4.53	5.18	4.95	5.09	5.29
JULY 1989	4.72	4.65	5.06	4.76	4.58	5.47	4.84	4.78	6.35
OCTOBER 1989	4.75	4.65	5.17	5.13	4.68	5.50	5.15	5.06	6.63
JANUARY 1990	5.40	4.78	5.17		4.78	5.45	4.99	5.05	5.09
APRIL 1990	4.86	4.55	5.05	4.55	4.63	5.19	4.78	4.66	4.92
JULY 1990	4.65	4.68	4.93	4.63	4.53	5.60	4.84	4.94	6.15
OCTOBER 1990	5.14	5.08	5.10	4.91	4.70	6.08	5.22	4.83	6.15
JANUARY 1991	4.64	4.70	4.79	4.37	4.79	5.39	5.01	5.13	5.71
APRIL 1991	4.82	4.70	4.95	4.50	4.82	5.37	4.86	5.14	5.33
JULY 1991	4.67	4.74	5.00	4.58	4.80	5.99	4.82	5.03	6.00
OCTOBER 1991	5.45	4.88	4.98	4.42	4.89	6.09	4.94	5.12	5.82
JANUARY 1992	4.96	4.81	4.78	4.15	4.70	5.20	4.94	5.03	5.30
APRIL 1992	5.06	5.14	5.20	4.33	4.91	5.52	4.80	5.24	6.61
JULY 1992	4.89	5.12	5.00	4.52	4.88	5.80	5.21	5.25	6.32
OCTOBER 1992	5.14	4.82	4.96	4.36	4.84	5.82	4.73	5.00	6.11

# PH TRENDS OF KETTLE PONDS

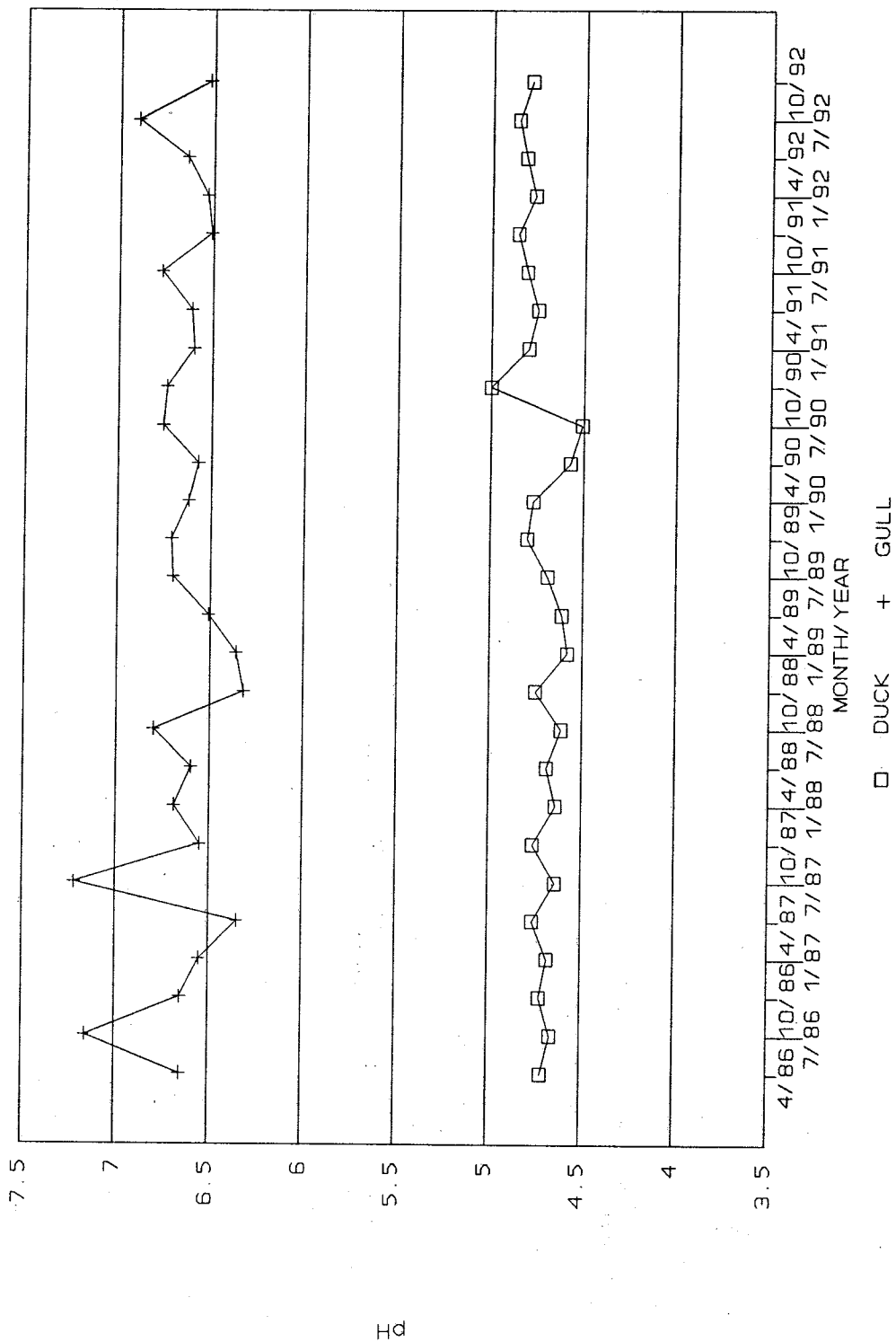


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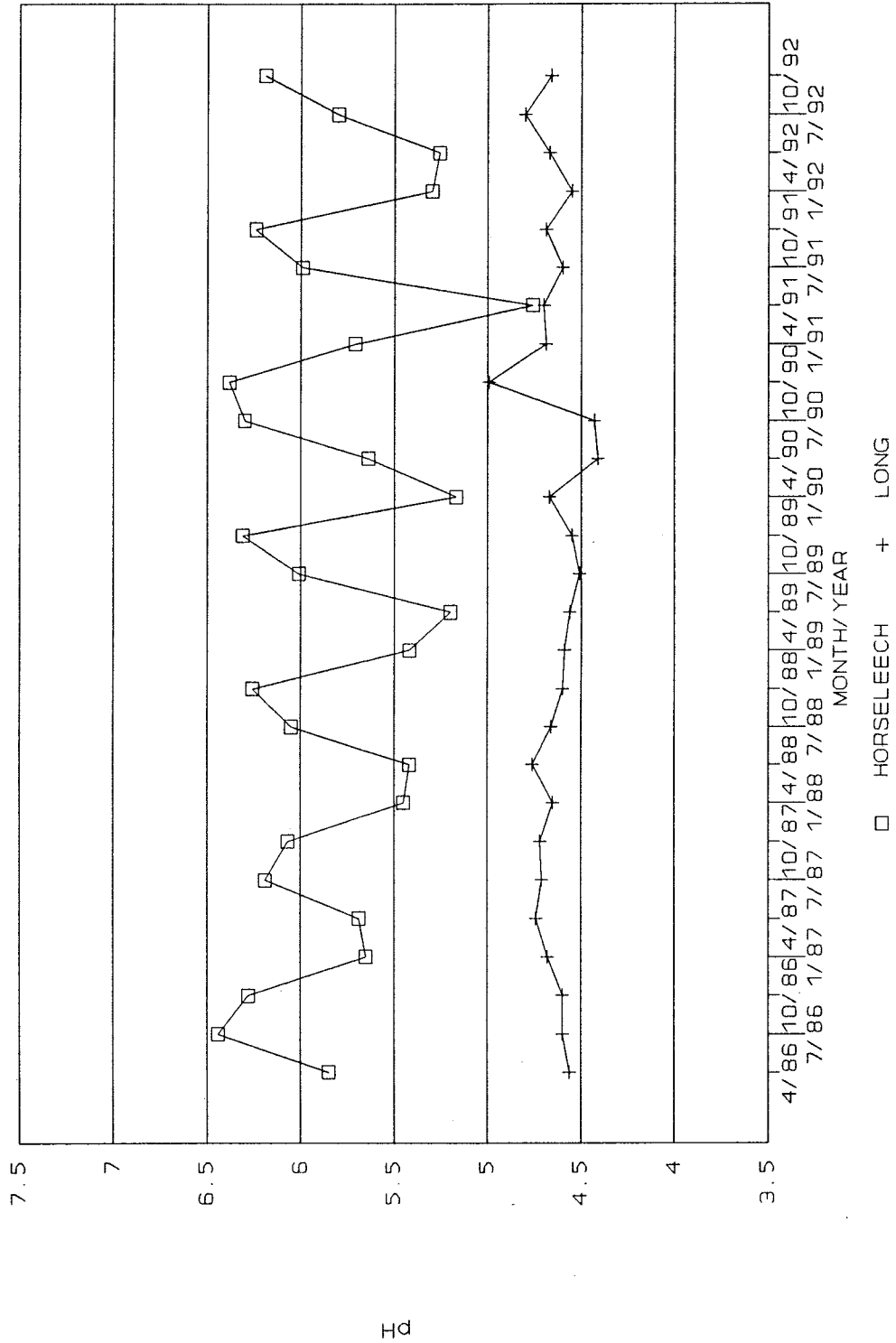




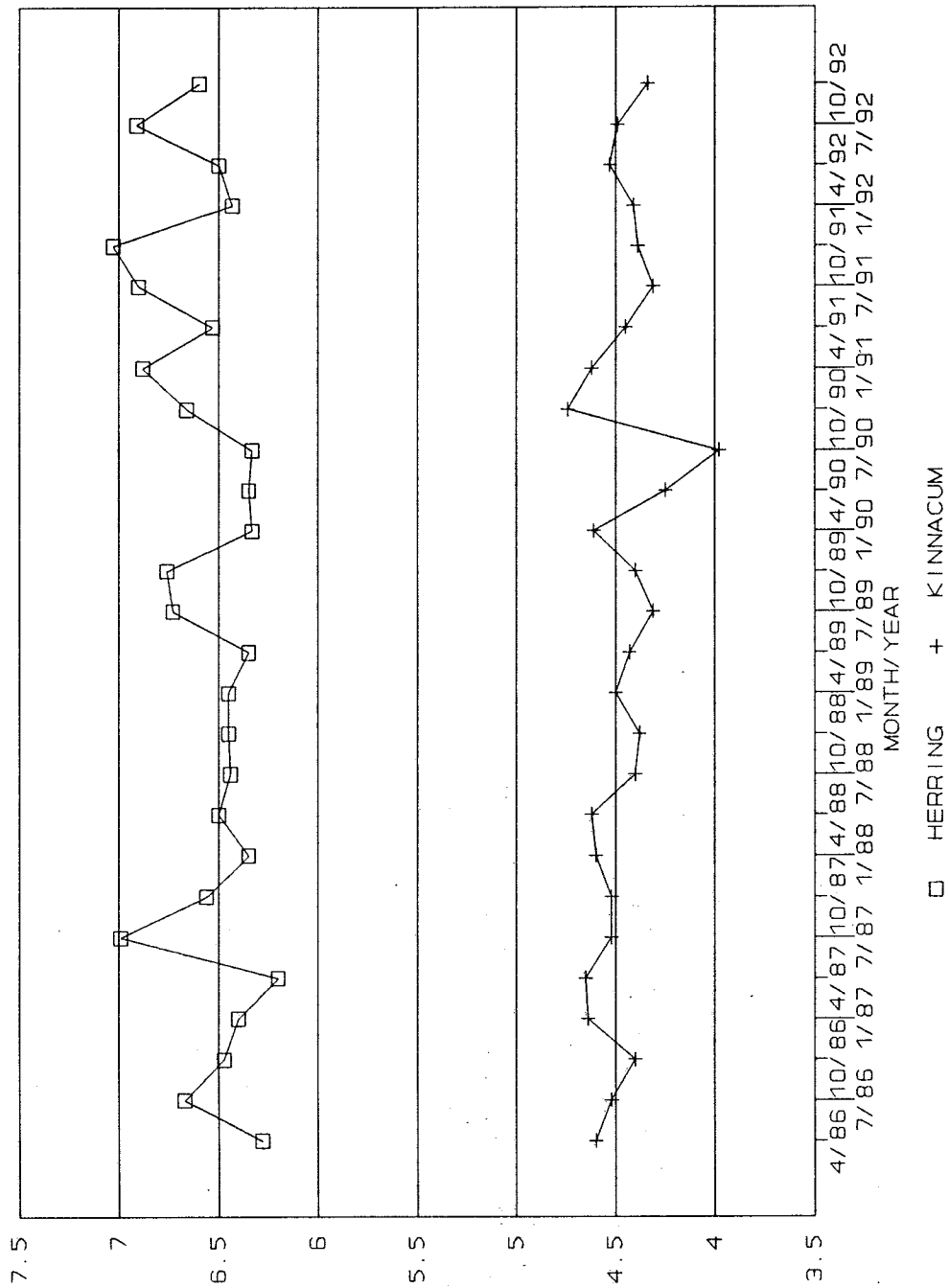
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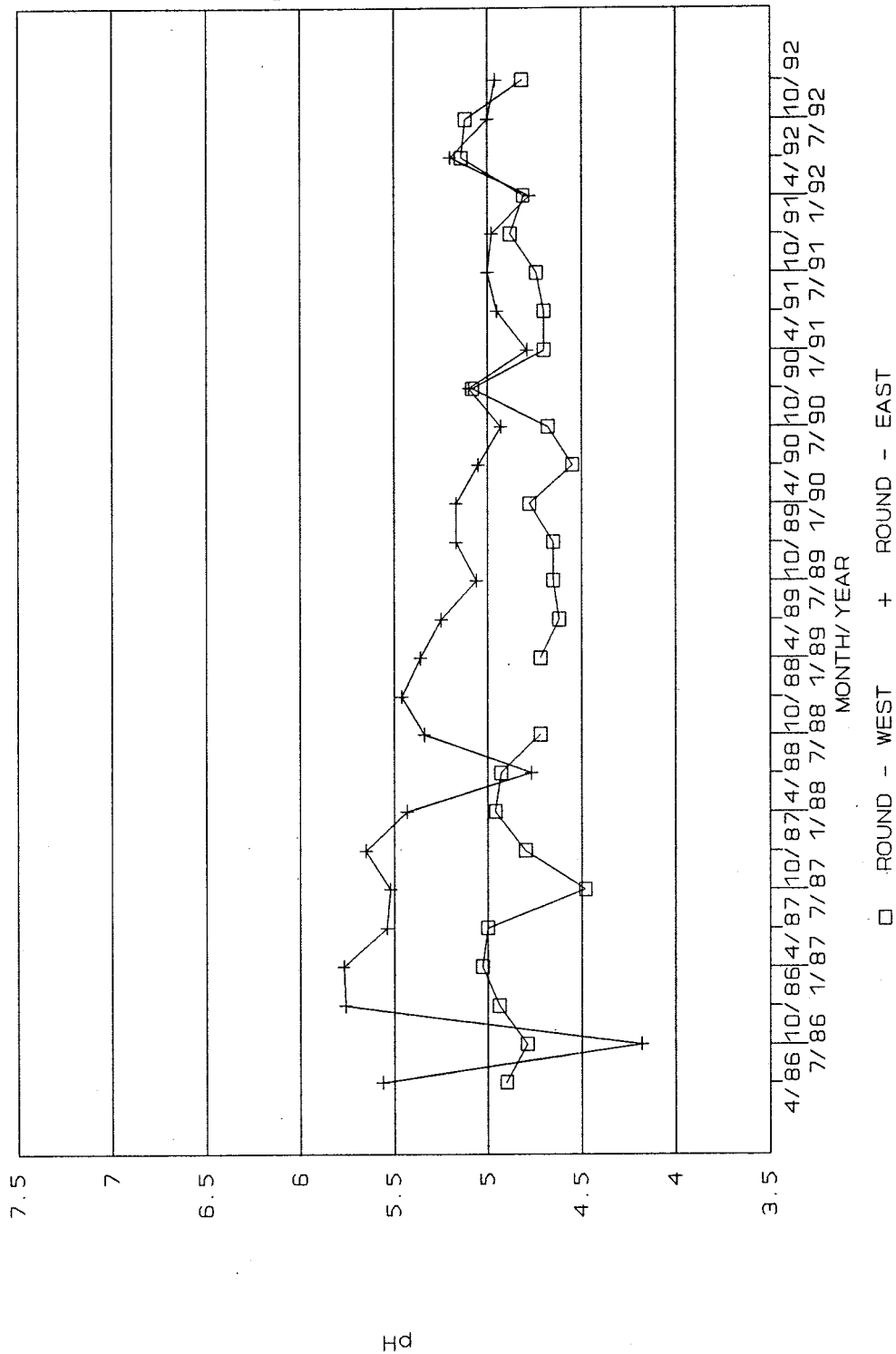
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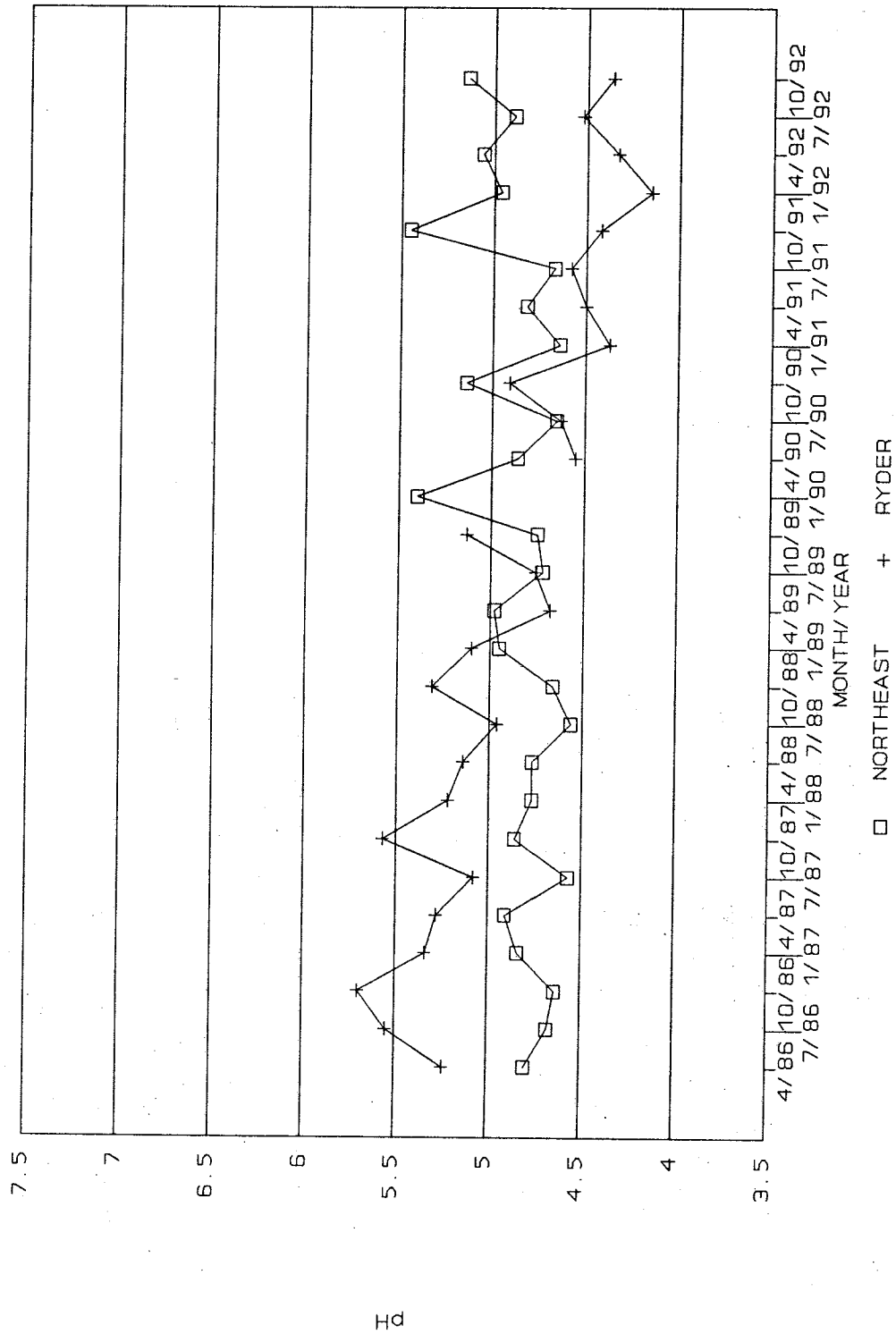
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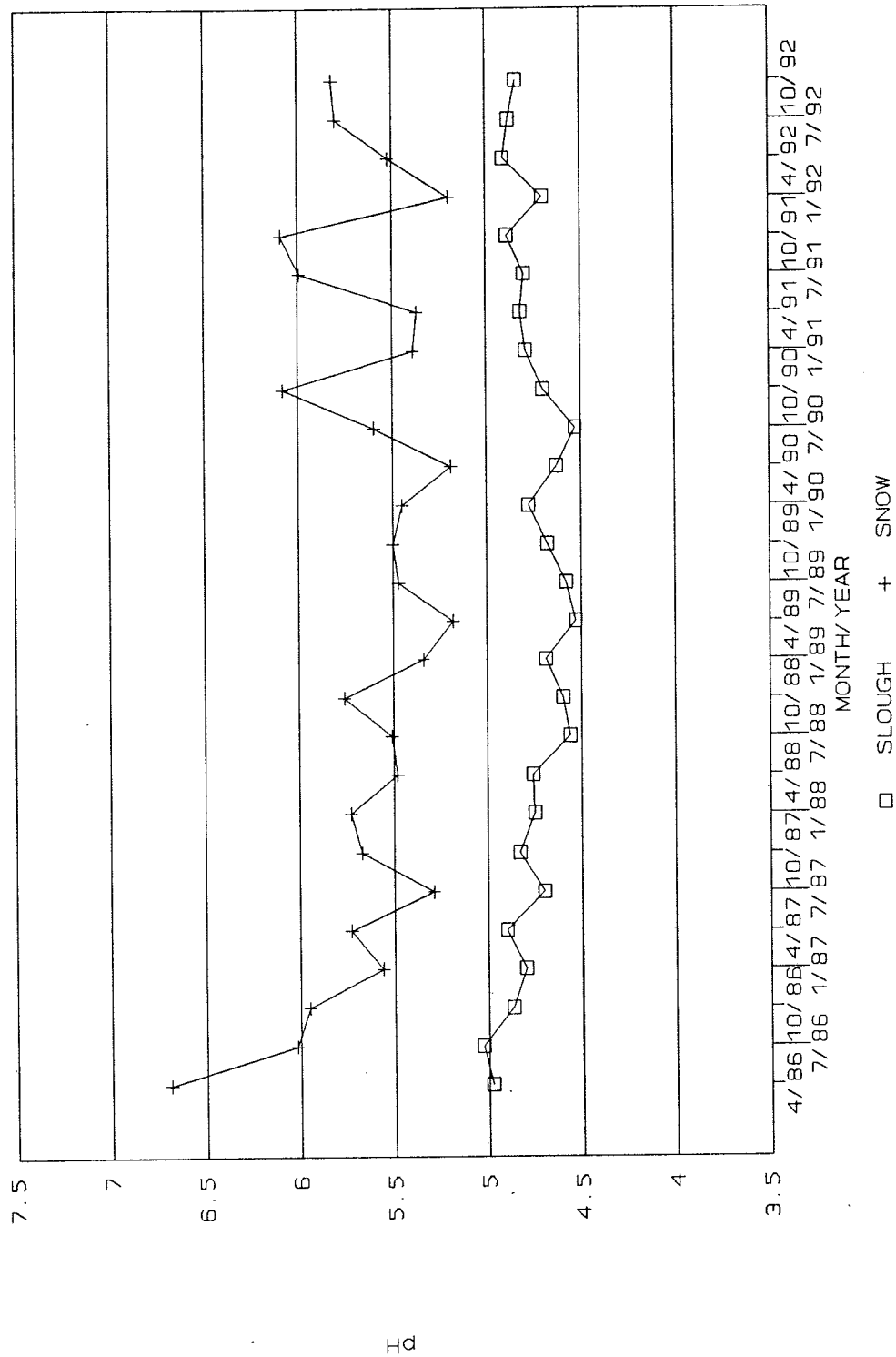
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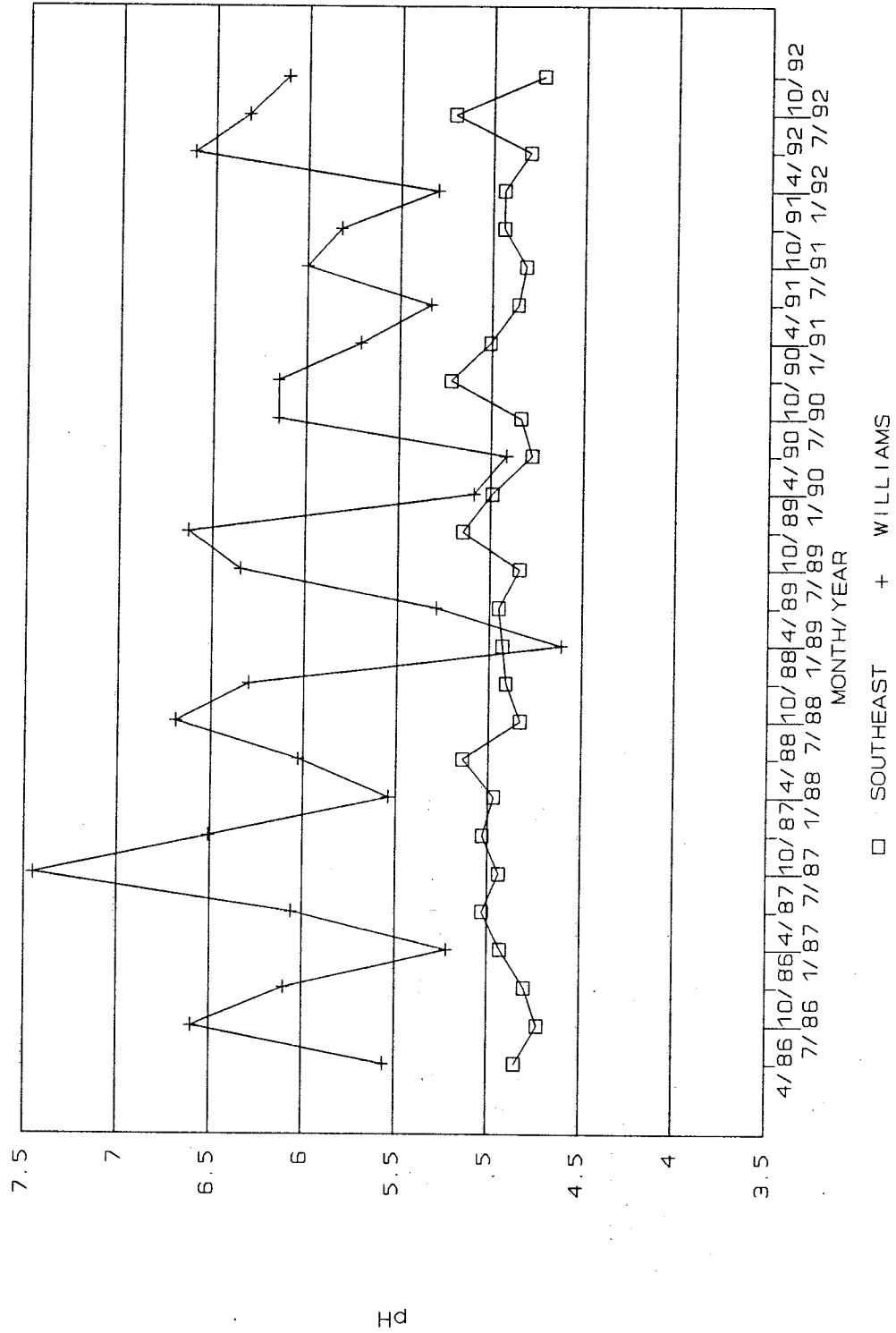
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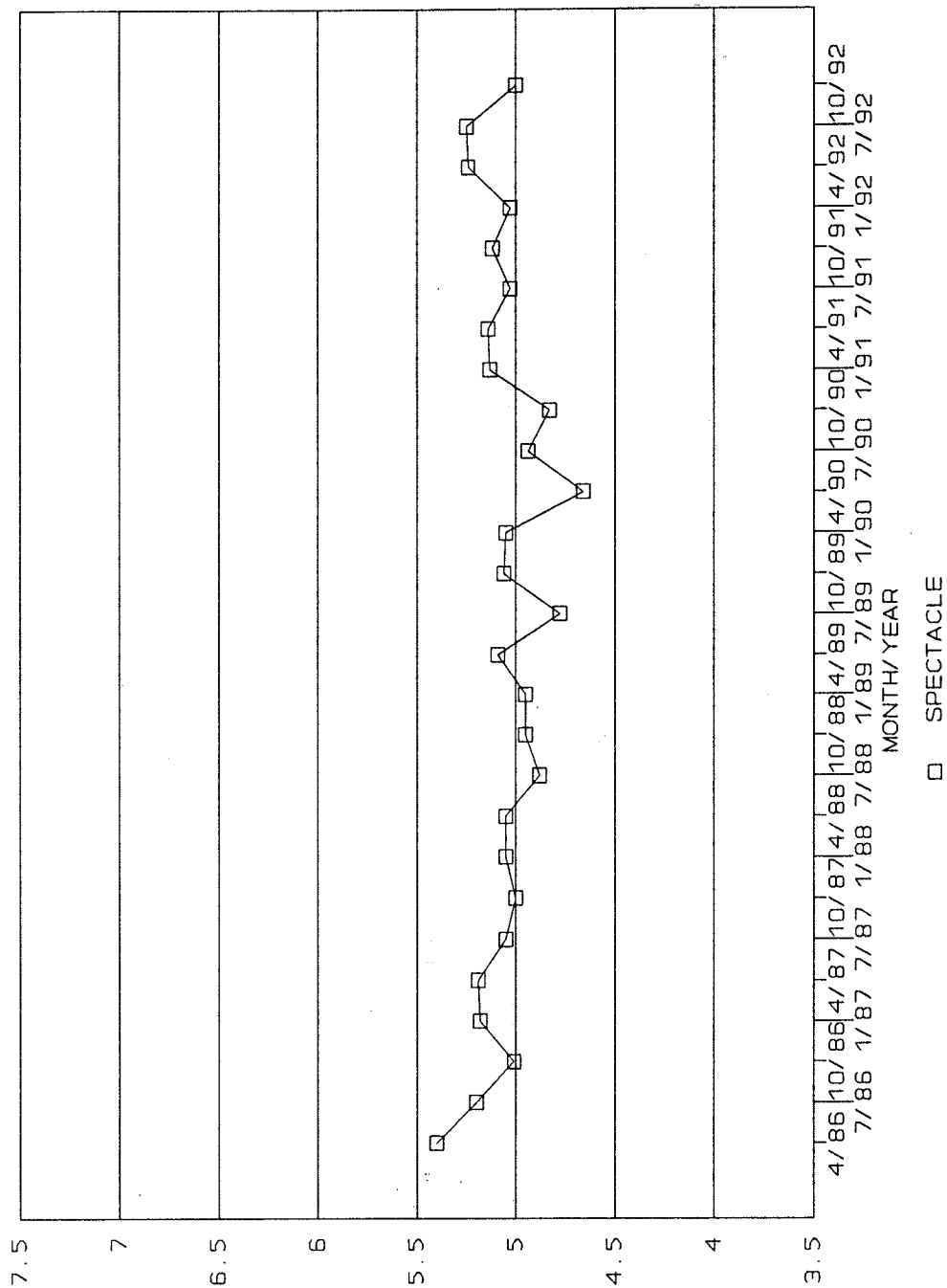
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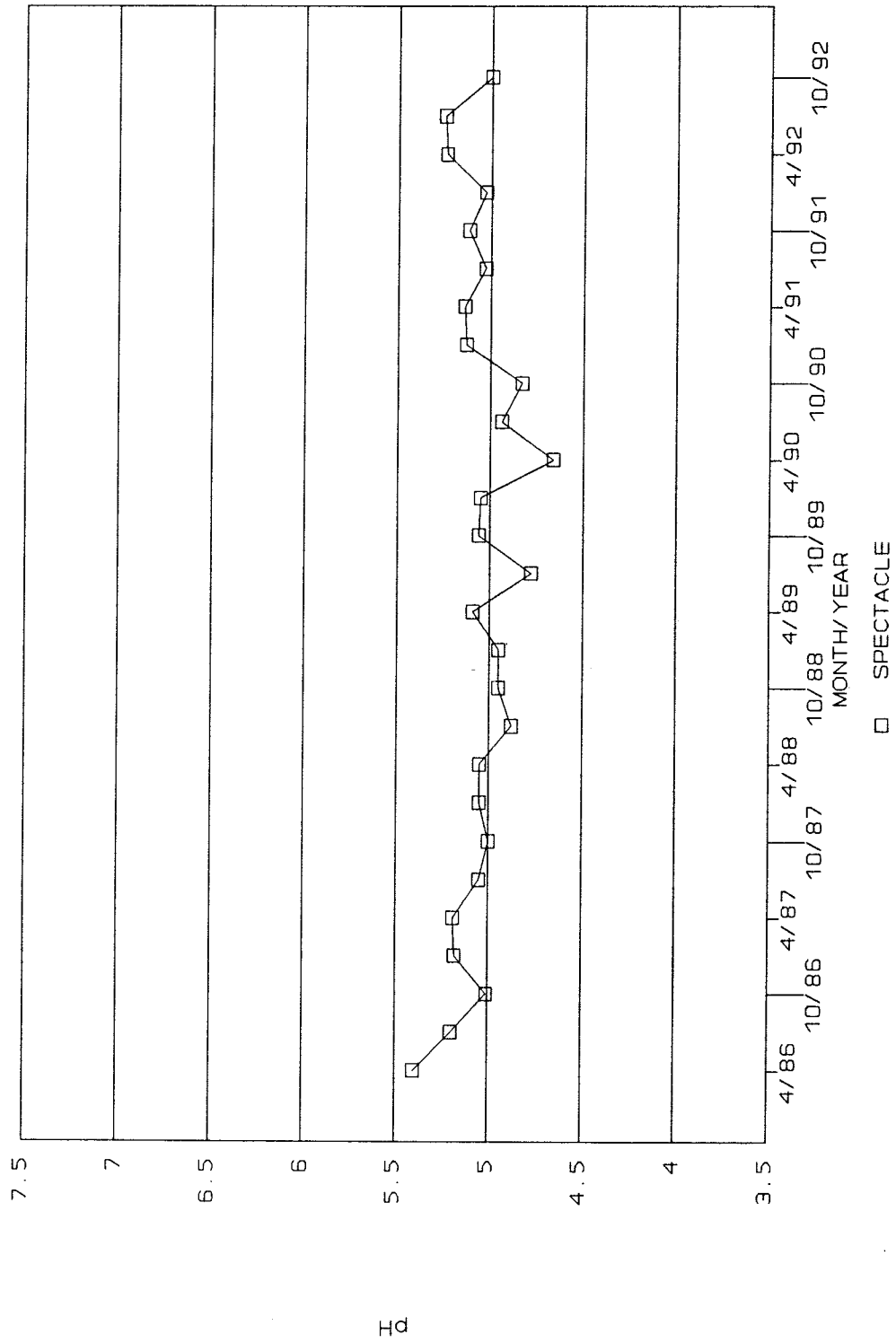


# PH TRENDS OF KETTLE PONDS





# PH TRENDS OF KETTLE PONDS





## APPENDIX 4

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### FIELD AND LABORATORY METHODS

## **Sampling**

All water samples are collected with a vertical Kemmerer bottle. Sample bottles were initially rinsed with 6N HCl, dedicated to specific pond and depth stations, and thereafter rinsed with distilled water between collections.

## **Preservation**

### **CATIONS**

A 60-ml polyethylene bottle is filled with sample and stored in an iced cooler. Upon arrival at the laboratory, five drops of trace metal grade  $\text{HNO}_3$  are added. This acidification keeps metals in solution and stable indefinitely; refrigeration is not necessary.

### **ANIONS**

A second 60-ml plastic bottle is filled with sample and refrigerated.

### **$\text{Fe}^{++}$ , TN, TP**

One 250 ml aliquot for  $\text{Fe}^{++}$ , total N, and total P is immediately acidified in the field to  $\text{pH} < 2$  with trace metal grade concentrated HCl. Since subsequent colorimetric analyses are very sensitive to pH, care must be taken to add only enough acid to lower pH below 2. (In April at the beginning of that year's sampling, empirically determine number of drops of acid needed for each pond's water.)

### **TOTAL SULFIDES**

Sulfides are highly unstable and quickly oxidized if exposed to air. Samples for total sulfides are fixed in the field with 3.2% zinc acetate. An aliquot of 5 ml of sample is quickly pipetted to a 20-ml scintillation vial containing 7.5 ml of 3.2% zinc acetate. These samples are stored on ice in the dark until analysis.

### **DISSOLVED OXYGEN**

Per the azide modification of the Winkler method, 1 ml each of manganous sulfate and potassium iodide sodium azide is added in the field to the sample contained in a 300 ml BOD bottle. The bottle is inverted several times to mix. The fixed sample can be stored for 24 hours provided the reservoir in the BOD bottle stopper is kept filled with water to prevent air entry.

## Laboratory Analyses

### FERROUS IRON

Put 10 ml of the acidified  $\text{Fe}^{++}$ , TN, TP sample in a 25 ml test tube. Add 0.2 ml 5.5 N HCl (trace metal grade only), followed by 0.2 ml ferrozine reagent (0.515 g/100 ml), and finally 0.2 ml of buffer (400g ammonium acetate + 350 ml  $\text{NH}_4\text{OH}$  diluted to 1 l). Measure absorbance after 1 min at 562 nm. Use ferrous ammonium sulfate to prepare calibration standards ranging from 0.05 to 2.0 ppm. The standard curve should be linear through 2.5 ppm.

### TOTAL SULFIDES

To the 5 ml samples fixed with ZnAc in scintillation vials in the field, add 10 ml of the indicator dye (DSDP = 3.728 g p-Aminodimethylaniline (a.k.a. n,n-dimethyl-p-phenylene diamine monohydrochloride) + 6.0 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  added to a 1-l volumetric flask topped to the mark with 6N HCl). Quickly cap to avoid loss of liberated  $\text{H}_2\text{S}$ . Shake the vial and place in the dark for color development for 45 min. Read absorbance against a distilled water reagent blank, treated exactly as a pond water sample, at 670 nm. Because reduced sulfur standards are difficult to prepare and maintain, use the following previously-derived relationship to calculate concentration:

$$\text{Conc. (mM)} = \text{Abs}/0.542 \times 0.1 = \text{Abs} \times .184$$

### TOTAL NITROGEN IN ALKALINE PERSULFATE DIGESTS OF PONDWATER

(Adapted from LACHAT QuikChem Method 30-107-04-1-B)

#### *Principle:*

The various species of nitrogen compounds dissolved in the sample (excluding dissolved nitrogen gas) are oxidized to nitrate by digestion with alkaline potassium sulfate. The nitrate is quantitatively reduced to nitrite by passage through a cadmium column. The nitrite is then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride (NED). The resulting water-soluble dye has a magenta color which is read at 520 nm.

#### *Glassware Handling:*

All glassware and containers, including digestion tubes and caps are rinsed with dilute HCl (about 1 M), followed by three rinses with DI water.

*Sample Digestion:*

1. Place 10.00 mL of the sample or standard solution into either a 30 mL or a 50 mL screw cap test tube.
2. Add 5.00 mL of potassium persulfate oxidizing agent (Reagent 1, below). Prepare immediately before use. Cap the tube securely.
3. Place tubes in a pressure cooker at 15 lb pressure for 30 minutes. Allow pressure to dissipate slowly. Remove tubes and allow to cool to ambient temperature.
4. Add 1.0 mL Reagent 2 (below), mix, and add 1.0 mL Reagent 3 (below). Mix briefly. Samples and standards are now ready for analysis.

*Reagents (Use DI water for all reagents):*

Reagent 1. Alkaline Persulfate Oxidizing Reagent.

Dissolve 9.0 g sodium hydroxide and 20.1 g potassium persulfate in about 700 mL of water. Dilute to the mark in a one liter volumetric flask and invert three times. Nitrogen contamination of the persulfate is a regular problem. Start with Baker InstraAnalyzed Grade (N supposedly <0.001%) and purify by the following method:

**Recrystallization of Potassium Persulfate.**

Dissolve 48 g of Baker persulfate (above) in 300 mL DI water in a 1000 mL Erlenmeyer flask. Heat with hand stirring and swirling to 65 degrees C until dissolved. Continue to heat with swirling to 75 degrees C. Remove from heat and immediately place in ice water to cool and induce the production of crystals. Using #40 Whatman qualitative paper, filter with 5 psi vacuum. Rinse, then dry and fluff crystals for five minutes. Store in a desiccator over calcium chloride.

Reagent 2. Hydrochloric Acid, 0.45 M

To a one liter volumetric flask in a FUME HOOD, add about 900 mL water and 37.5 mL concentrated hydrochloric acid (37%, ASC Reagent Grade,  $d=1.200$ ). Dilute to the mark and invert three times.

Reagent 3. Borate Buffer, 1.0 M, pH 7.5

Dissolve 61.8 g boric acid and 8.0 g sodium hydroxide in about 800 mL of water, Mix on a magnetic stirrer for at least four hours. Dilute to the mark in a one liter volumetric flask and invert three times.

Reagent 4. 15 M Sodium Hydroxide

SLOWLY AND CAUTIOUSLY add 150 g NaOH to 250 mL water. The solution will get very hot. Stir until dissolved. Cool and store in a plastic bottle.

Reagent 5. Ammonium Chloride Buffer, pH 8.5

To a one liter volumetric flask IN A FUME HOOD, add 500 mL water, 105 mL concentrated hydrochloric acid, 95 mL ammonium hydroxide, and 1.0 g disodium EDTA. Stir to dissolve, then dilute to the mark and invert three times. Adjust to pH 8.5 if necessary.

Reagent 6. Sulfanilamide Color Reagent

To about 600 mL water, add 100mL 85% phosphoric acid, 40.0 g sulfanilamide, and 1.0 g N-(1-naphthyl)-ethylenediamine dihydrochloride (NED). Shake to wet and stir with a stir bar for at least 30 minutes. Pour into a one liter volumetric flask and dilute to the mark; invert three times. Filter and store in a dark bottle. Stable for one month.

Reagent 7. Carrier solution.

DI water.

Reagent 8. Cadmium Column (Purchased from LACHAT)

*Preparation of Standards:*

Standard 1. Stock Nitrate Standard 1000. mg N/L as nitrate.

In a one liter volumetric flask, dissolve 7.218 g potassium nitrate in about 600 mL water. Add 2 mL chloroform. Dilute to the mark and invert three times. This solution is stable for one month.

## Standard 2. Intermediate Stock Standard 10.0 mg N/L

In a one liter volumetric flask add exactly 10.00 mL Standard 1 to about 900 mL water, dilute to the mark and invert three times.

## Standard 3. Working Stock Standard 1.00 mg N/L

In a 250 mL volumetric flask, dilute 25.0 mL Standard 2 to the mark and invert three times.

## Set of 5 Working Standards: 1.00, 0.80, 0.40, 0.20, 0.05 mg N/L

To four 100 mL flasks add, respectively: 80.0, 40.0, 20.0, 5.0 mL Standard 3. Dilute each to the mark and invert three times.

**Note:** This range of standards has been useful for Cape Cod kettle ponds. If samples always fall within a narrower range, more standards can be added within this range and the others may be dropped.

### *Timing:*

Sample throughput:	50 samples per hour 72 seconds per sample
Pump speed:	35
Cycle period:	72 seconds
Inject to start of peak period:	24 seconds
Inject to end of peak period:	94 seconds

### *System Notes:*

1. The cadmium column efficiency should be above 90% if working properly. To check this, inject first a nitrate standard, followed by a comparable nitrite standard. The ratio of nitrate/nitrite x 100% is the efficiency.
2. Set the Presentation, Data Window, Top Scale Response to 0.30.
3. If this method is to be used for saline waters, consult the LACHAT method 30-107-04-1-b for artificial seawater diluents.
4. For Manifold Diagram, see LACHAT method.



## TOTAL PHOSPHOROUS - ACID PERSULFATE DIGESTION

(Adapted from LACHAT QUIKCHEM # 10-115-01-1-F)

### *Principle:*

All forms of phosphorus are converted to orthophosphate by this method. The orthophosphate ion ( $\text{PO}_4^-$ ) reacts with ammonium molybdate and antimony potassium tartrate under acidic conditions to form a blue complex which absorbs light at 880 nm.

**Note:** The method is extremely sensitive to pH in the sample. The higher the acidity, the less sensitive the method.

### *Sample Handling:*

Samples are kept cold in the field, then frozen until they can be analyzed. Alternatively, samples can be acidified to  $\text{pH} < 2$  with trace metal grade HCl.

### *Sample Digestion:*

Add 0.5 ml 30%  $\text{H}_2\text{SO}_4$  and 1.0 ml persulfate solution (below) to a 25 ml sample in a 50 mL screw cap test tube. Cap the tube securely.

**Persulfate solution:** Dissolve 20 g ammonium peroxydisulfate [ $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ] in water to the mark in a 100 ml volumetric flask. Make this reagent fresh daily, just before using.

When all samples and standards have been prepared in this manner, place them in a pressure cooker set at 15 lb and process for 30 minutes. Allow pressure to dissipate slowly, then remove tubes and allow to cool to ambient temperature.

### *Reagent Preparation:*

Use deionized water for all solutions.

**Note:** De-gassing with Helium. To prevent bubble formation, de-gas all the following solutions except the standards with helium. Bubble He vigorously through the solutions for one minute. De-gas ascorbic acid reducing solution before adding dodecyl sulfate.

### Reagent 1. Stock Ammonium Molybdate Solution

Dissolve 40.0 g of ammonium molybdate tetrahydrate in approximately 800 mL of water; then dilute to the mark in a one liter volumetric flask and invert three times to mix. Store in plastic and refrigerate.

### Reagent 2. Stock Antimony Potassium Tartrate Solution

Dissolve 3.0 g antimony potassium tartrate hemihydrate in approximately 800 mL water. Dilute to the mark in a one liter volumetric flask and invert three times. Store in a dark bottle and refrigerate.

### Reagent 3. Molybdate Color Reagent

To about 500 mL water, slowly and CAUTIOUSLY add 20.9 mL concentrated sulfuric acid. Swirl to mix. When the solution becomes cool enough to handle comfortably, add 72.0 mL Reagent 2 and 213.0 mL Reagent 3. Dilute to the mark in a one liter volumetric flask and invert three times.

### Reagent 4. Ascorbic Acid Reducing Solution

In about 700 mL water, dissolve 60.0 g ascorbic acid; dilute to the mark in a one liter volumetric flask and invert three times. Prepare fresh weekly.

### Reagent 5. Sodium Hydroxide- EDTA Rinse

Dissolve 65 g sodium hydroxide and 6 g tetrasodium ethylene diamine tetraacetic acid in one liter of water.

### Reagent 6. Carrier Solution

The carrier solution is DI water plus sulfuric acid made up to match the sample and standard solutions, for example, one mL 30% sulfuric acid plus 52 mL water. A convenient amount to make up might be 15 mL acid plus 780 mL water. REMEMBER TO ADD ACID TO WATER.

### *Preparation of Standards:*

#### Standard 1. Stock Standard 100 mg P/L

In a one liter volumetric flask dissolve 0.4394 g primary standard grade anhydrous potassium dihydrogen phosphate (dried at 105 degrees C) in about 800 mL water. Dilute to the mark and invert three times.

## Standard 2. Working Stock Standard 1000 ug P/L

In a one liter volumetric flask, dilute 10.0 mL Standard 1 to the mark with water and invert three times.

### Set of Five Working Standards: 200, 100, 50, 25, 10 ug P/L

To five 100 mL volumetric flasks add, respectively: 20.0, 10.0, 5.0, 2.5, 1.0 mL Standard 2. Dilute each to the mark with water and invert three times.

**Note:** Digest the samples and standards as directed in Sample Digestion above.

### *Timing:*

Sample throughput;	83 samples per hour
	43 seconds per sample
Pump speed:	35
Cycle period:	43 seconds
Inject to start of peak period:	10 seconds
Inject to end of peak period:	49 seconds

### QuikChem AE Settings:

Data Window:      Top Scale Response: Approximately 0.08 abs  
                         Bottom Scale Response: 0.00

### *System Notes:*

1. Allow 15 minutes for the heating unit to warm up to 37° C.
2. At the end of the run, place the color reagent and ascorbic acid transmission lines into the NaOH-EDTA solution, Reagent 5. Pump this solution for approximately 5 minutes to remove any precipitated reaction products. Then place these lines in DI water and pump for an additional 5 minutes. Pump all lines dry.
3. For manifold diagram, see QuikChem Method 10-115-01k-1-F.



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As the nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural and cultural resources. This includes fostering wise use of our land and water resources, protecting our fish and wildlife, preserving the environmental and cultural values of our national parks and historical places, and providing for the enjoyment of life through outdoor recreation. The department assess our energy and mineral resources and works to ensure that their development is in the best interest of all our people. The department also promotes the goals of the Take Pride in America campaign by encouraging stewardship and citizen responsibility for the public lands and promoting citizen participation in their care. The department also has a major responsibility for American Indian reservation communities and for the people who live in island territories under U.S. administration.